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Proceedings of the Technical Seminar on Chemical Spills

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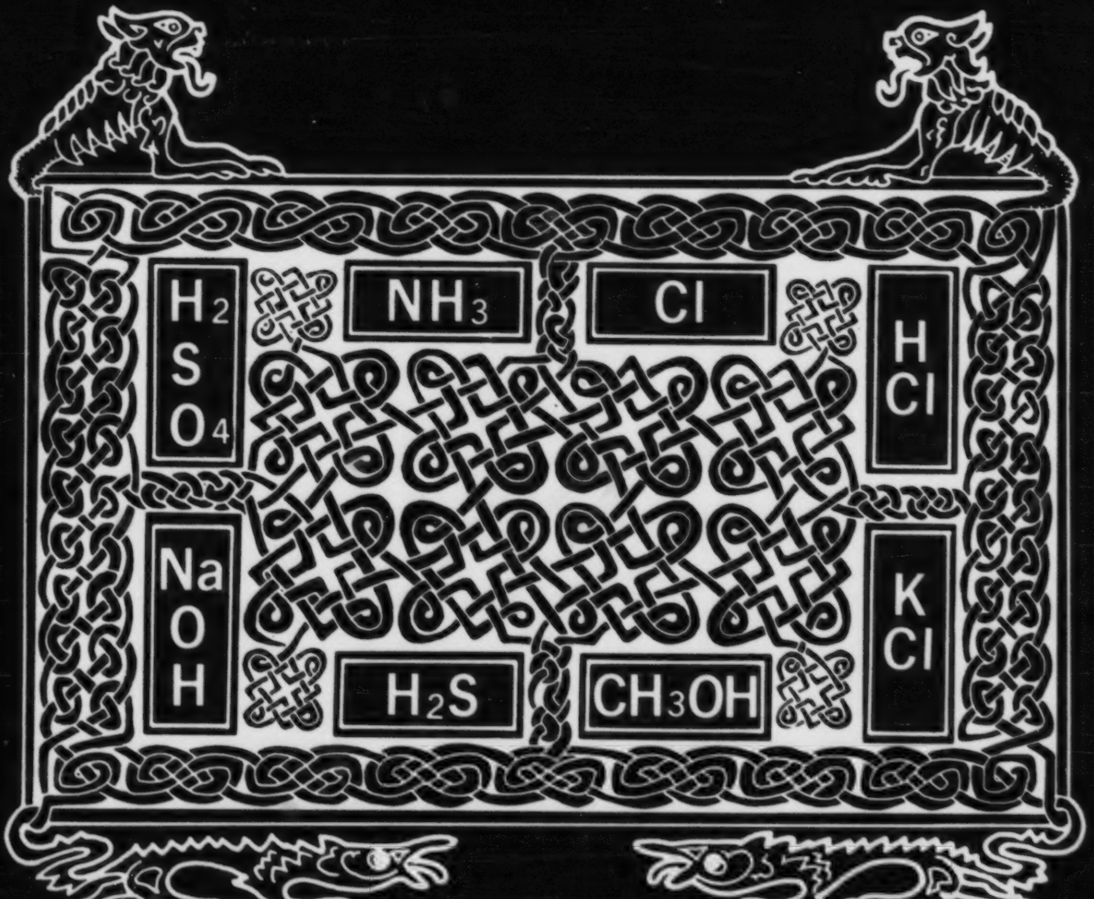
H_2SO_4
NH_3
Cl
HCl
NaOH
H_2S
CH_3OH
KCl

Canada

PROCEEDINGS

OF THE

THIRD ANNUAL

TECHNICAL SEMINAR

ON CHEMICAL SPILLS

SEMINAR SPONSORED BY THE
TECHNICAL SERVICES BRANCH,
ENVIRONMENTAL PROTECTION SERVICE,
ENVIRONMENT CANADA

FEBRUARY 5-7, 1986
MONTREAL, QUEBEC

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TABLE OF CONTENTS

PAGE

SESSION I CHEMICAL/PHYSICAL PROPERTIES AND MODELLING

MODELLING OF THE SPREADING, INFILTRATION AND EVAPORATION OF CHEMICAL SPILLS ON GRASS AND IMPERMEABLE SURFACES 1

R. Belore
S.L. Ross Environmental Research
Ottawa, Ontario

E. McBean and G. Farquhar
University of Waterloo
Waterloo, Ontario

SUBSURFACE CONTAMINATION FROM SPILLS OF DENSE NON-AQUEOUS PHASE LIQUID (DNAPL) 11

S. Feestra
Zenon Environmental
Burlington, Ontario

HAZARD ASSESSMENT OF AQUATIC ORGANISMS EXPOSED TO CHEMICALS AFTER AN ACCIDENTAL SPILL FROM BULK TANKERS AT SEA 23

C.J.M. Wolff and C.L.M. Poels
Shell International Petroleum
The Hague, The Netherlands

HEAVY GAS DISPERSION MODELLING FOR HAZARD AND RISK ASSESSMENT 41

E. Alp, C.P. Bourque, M. Oliverio and R. Portelli
Concord Scientific
Downsview, Ontario

D.H. Napier
University of Toronto
Toronto, Ontario

A COMPUTER MODEL FOR PREDICTING OUTFLOW RATES FROM DAMAGED CHEMICAL STORAGE AND TRANSPORTATION TANKS 57

I.A. Buist and R. Belore
S.L. Ross Environmental Research
Ottawa, Ontario

HAZARD ANALYSIS OF PROPANE TANK CAR FAILURES IN A SPECIFIC LOCATION 81

J.S. Klement and D.H. Napier
University of Toronto
Toronto, Ontario

SPREADING OF CHEMICALS ON ICE AND SNOW 99

P. Kawamura and D. Mackay
University of Toronto
Toronto, Ontario

PAGE

DEUX SYSTEMES INFORMATISES POUR LA PREVISION DU COMPORTEMENT DES POLLUTIONS EN MILIEU MARIN 109

S. Scory
Ministère de la Santé Publique
Liège, Belgique

SOURCE TERMS FOR DISPERSION MODELLING OF RELEASES OF HEAVY GASES 111

D.H. Napier
University of Toronto
Toronto, Ontario

M. Oliverio and E. Alp
Concord Scientific
Downsview, Ontario

A PERSPECTIVE ON THE BEHAVIOUR OF CHEMICALS SPILLED IN SOIL 123

D. Mackay
University of Toronto
Toronto, Ontario

G.E. Hoag
University of Connecticut
Storrs, Connecticut

SESSION II COUNTERMEASURES

THE DEVELOPMENT OF A DISCIPLINED APPROACH FOR EMERGENCY RESPONSE 143

W.F. Mackay
Esso Chemical Canada
Toronto, Ontario

R.H. Goodman
Esso Resources Canada
Calgary, Alberta

APPLICATIONS DE LA TECHNOLOGIE DES MEMBRANES DANS L'OUEST CANADIEN 151

J. Tremblay
Environnement Canada
Ottawa, Ontario

MEMBRANE TECHNOLOGY APPLICATIONS IN WESTERN CANADA 181

J. Tremblay
Environment Canada
Ottawa, Ontario

UTILISATION DE L'OSMOSE INVERSE ET DE L'ULTRAFILTRATION AUX MUNICIPALITES DE GRANBY ET STE-ANNE-DES-PLAINES (QUEBEC) 207

B. Beauregard
Environnement Québec
Montréal, Québec

J. Tremblay
Environnement Canada
Ottawa, Ontario

PAGE

IN-SITU TREATING AGENTS FOR CHEMICAL SPILLS 225

L.B. Solsberg
Hatfield Consultants
Vancouver, British Columbia

A. Maynard
ASL Analytical Service Labs
Vancouver, British Columbia

SESSION III ANALYTICAL TECHNIQUES AND SAFETY

CONTINUING DEVELOPMENT OF A VEHICLE-PORTABLE ANALYTICAL SYSTEM 237

A.M. Bobra
Environment Canada
Ottawa, Ontario

SUMMARY OF U.S. EPA, OERR, FIELD OPERATING PROCEDURES (FSOP'S) 243

R.D. Turpin
U.S. Environmental Protection Agency
Edison, New Jersey

THE UTILITY OF FULLY ENCAPSULATING CHEMICAL PROTECTION SUITS IN U.S. COAST GUARD CHEMICAL SPILL RESPONSE 249

S.J. O'Malley and J.O. Stull
U.S. Coast Guard
Washington, D.C.

CONTINUING DEVELOPMENT OF A PERSON-PORTABLE ANALYTICAL SYSTEM 261

M. Townshend Colford
Hatfield Consultants
Vancouver, British Columbia

SESSION IV POLYCHLORINATED BIPHENYLS - PCBs

EVAPORATION FROM PCB MIXTURES 279

P.K. Misra and R. Bloxam
Ministry of the Environment
Rexdale, Ontario

PAGE

CLEANUP OF PCBs FROM ABANDONED DEW LINE SITES 299

S. Ponton
Department of National Defense
Westwin, Manitoba

REMEDIATION OF PCB CONTAMINATION IN THE KIWANIS PARK SECTION OF POTTERSBURG CREEK IN LONDON, ONTARIO 307

R.J. Rush, J.R. Bray and D.E. Metcalfe
Canviro Consultants
Kitchener, Ontario

THE ORGANIZATION OF A LARGE SCALE DECONTAMINATION OPERATION 321

J. Paquin
Sanexen International
Montreal, Quebec

SESSION V RECENT SPILL EXPERIENCES

THE KEY LAKE SPILL 325

M.B. Zgola
Atomic Energy Control Board
Ottawa, Ontario

VERONA WELL FIELD, GROUND WATER CLEANUP ACTION, BATTLE CREEK, MICHIGAN 347

D.M. Caplice
U.S. Environmental Protection Agency
Chicago, Illinois

T.H. Defouw
Fruehauf Corporation
Detroit, Michigan

STELLAKO SPILL - A DIFFICULT RESPONSE PROBLEM 371

D.F. Brown and A.C. Williams
Ministry of the Environment
Prince George, British Columbia

OTHER SESSION PAPERS 379

Modelling of the Spreading, Infiltration and Evaporation of Chemical Spills on Grass and Impermeable Surfaces

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INTRODUCTION

Research is currently underway to develop and validate mathematical models to predict the behaviour of chemical spills on grass and impermeable surfaces, under sponsorship of the Environmental Emergencies Technology Division (EETD) of Environment Canada.

During the development of the EnviroTIPS manuals by EETD it was found that existing spreading models were not suitable for application to chemical spills on land. This modelling is important since the spreading of the chemcal greatly affects both the evaporative flux and the infiltration rate of the chemical into the soil. A poor prediction of the chemical's pool size (by an inappropriate spreading model) also results in errors in the modelling of the dispersion of the chemical in air and soil. Inaccurate estimates of potential health hazard zones surrounding the spill site can then result. This could lead to inappropriate, or even dangerous action, by response personnel.

The development and validation of a more accurate model of the spread of chemicals on land is the subject of this paper. The mathematical model development being conducted is a continuation of the work reported by Farquhar and McBean (1984) and Allan et al (1985). To test the validity of the models being developed, relatively large scale laboratory tests are being conducted in S.L. Ross's laboratory in Ottawa. The results of the experimental program are being used to calibrate and validate the simulation models. Descriptions of the mathematical models being developed and the experimental program being conducted, follow. A comparison of model outputs to some of the preliminary spreading data that has been collected in the laboratory is also presented.

MATHEMATICAL MODELLING

An extensive review of the published literature pertaining to the modelling of chemical spills on land has been conducted. The following is a very brief synopsis of the findings of this literature search as well as a description of the model being developed in this study.

Shaw and Briscoe (1978) reviewed models that simulate the spill of cryogenic liquids on water and soil. The majority of these models assume an instantaneous radial spill, and that the spill volume at any time is contained in a sequence of collapsing cylinders. Abbott (1961), Fay (1969), Hoult and Suchon (1970) and Fannelop and Waldman (1971) have all developed theories and analytical models to explain the spreading of oil over calm water. Unfortunately these models are not applicable to spills on land.

Wall (1984) developed a very complicated model to simulate the spread of chemicals over soil. The model, which accounts for supercritical flow, a spontaneous hydraulic jump, subcritical flow and a moving bore, combined with a time-dependent inflow boundary, presents extensive numerical concerns. The model uses an explicit finite difference MacCormack scheme to numerically solve the spill equations, but the computational requirements are large. For this reason the model cannot be considered practical for spill response purposes.

Raisbeck and Mohtadi (1974) developed a model to simulate the spread of petroleum products, over both permeable and impermeable Arctic soils. They assumed that the oil slick reaches and maintains an equilibrium height which, on smooth surfaces, is a function of the interfacial phenomena. A major advantage of this model is it's simplicity, however, the assumption of constant height could result in considerable error since it does not reflect the roughness of the surface over which the liquid flows.

The model developed within this study initially assumes the downstream depth to be determined by surface affinity effects, as per Raisbeck and Mohtodi. Then, using an integrated version of the standard step method (as per Streeter and Wylie, 1981), a backwater profile computation is undertaken, as schematically depicted in Figure 1. The length of the backwater profile is obtained through an iterative procedure. The predicted length is established when the volume of liquid under the profile matches that which has been spilled. This backwater calculation incorporates the surface roughness component omitted in Raisbeck's and Mohtadi's model.

If the quantity of liquid spilled is small, the surface affinity depth is larger than the critical depth and the calculation steps outlined above, proceed appropriately. However, if the quantity of liquid spilled is large, the critical depth exceeds the surface affinity depth. The net results of this condition is that if the boundary condition is taken as per Figure 1, the backwater calculation will not proceed along the classical M1 profile (eg. see Henderson, 1966). Under these circumstances the backwater calculations must proceed from the critical depth. To identify the location of the moving bore, the slope of the water surface upgradient from the critical depth is then used to extrapolate (by straight line) to the surface affinity depth and therefore the location of the bore.

The resulting model is very simple numericaly and can readily be solved on a microcomputer.

EXPERIMENTAL PROGRAM

The majority of the tests to generate data to compare with the mathematical model, are being conducted in the full-scale 2-dimensional test bed illustrated in Figure 2. The basin has a perforated bottom to prevent flooding of the soil layer and to allow the measurement of the quantity of chemical infiltrating through the soil. The 2-dimensional tests include the addition of chemical to both horizontal and sloped surfaces (see Figure 2). For the horizontal tests, the chemical source is applied to the centre of the surface with measurements being taken at both sides of the source for duplication of results. In the sloped tests the chemical is applied to the elevated end of the platform with measurements made downstream from the source.

A small number of tests are also being conducted in the 3-dimensional test facility illustrated in Figure 3. Infiltration, chemical depth and spreading rate are measured radially from a central chemical source in these experiments.

Test Conditions

Tests are being conducted with various combinations of the following conditions.

1)	surface type;	i)	natural sod placed over compacted topsoil
		ii)	plywood to simulate an impermeable soil condition
2)	flow rate;	i)	20 litres/minute,
		ii)	50 l/min., or
		iii)	80 l/min.
3)	chemical type;	i)	water,
		ii)	water doped with Carboxy Methyl Cellulose (CMC) to approximately 5 centistokes
		iii)	water doped with (CMC) to 15 centistokes, or
		iv)	a low boiling point chemical (to be selected).
4)	test bed slope;	i)	horizontal or
		ii)	sloped 10° from horizontal.
5)	test configuration;	i)	2-dimensional or
		ii)	3-dimensional

Test Methods

The following steps are taken in the tests completed on plywood.

i) The chemical source is positioned and the appropriate flow rate set by adjusting the area of the discharge opening. A constant head tank is utilized to maintain a constant flow rate throughout the test.

ii) Flow depth markers positioned along the centre-line of the flow path are coated with a water-indicating paste. This paste changes colour when in contact with water and thus permits the measurement of the "high-water" profile after the test is completed.

iii) The flow is then started and the chemical's spreading rate determined by timing the arrival of the chemical front at each of the flow depth markers.

iv) When the chemical reaches the end of the test bed the flow rate is stopped.

v) The maximum water depth profile reached during the test is then measured from the flow depth markers and the test bed is dried for the next test.

The tests conducted on the natural sod surface are somewhat more involved and require the following major steps:

i) Soil is placed in the test bed in 2 separate 7.5 cm lifts compacted each time by passing a weighted roller over the levelled surface (finished depth approximately 15cm).

ii) After the second layer is placed and rolled, the surface receives a final levelling to ensure an even flow of chemical to either side of the source.

iii) The sod is placed over the soil and rolled in place to improve the contact between the sod and soil.

iv) A corner of the sod is then lifted and a core sample of soil is taken and weighed to provide a pre-test measure of the soil's bulk density and porosity.

v) The sod surface is "broomed" to create a consistent surface roughness between tests.

vi) Flow depth markers are placed in the sod and coated with water-indicating paste (as in the plywood tests).

vii) Electrical conductivity probes are placed at 1 metre intervals along the flow's path on the sod surface, in the centre of the soil layer and at the bottom of the soil layer. These are connected to a computer data acquisition system described elsewhere (Belore, 1981). The time at which chemical passes by each probe is measured and recorded by the computer. Surface spreading and infiltration rates are measured automatically by this system.

viii) The chemical source is positioned and adjusted for the appropriate flow rate, as in the plywood tests.

ix) The flow is started and the chemical spreading rate measured manually as a check of the automated system and also as a precaution in the event of a failure of the automated system.

x) The flow is stopped after 200 litres of chemical is applied.
xi) The water depth profile is measured from the depth markers.
xii) The quantity of water which runs out the ends of the test basin is measured as is the quantity which infiltrates through the complete soil layer.
xiii) Finally a second set of soil core samples is taken to determine post-test soil conditions.
xiv) The saturated soil is then discarded and a new soil layer placed in the test bed to ensure similar soil conditions between tests.

RESULTS

Results of the physical and mathematical experiments indicative of the findings to date, are summarized in Figures 4 through 7, and Table 1. Comparisons of the location of the moving bore as a function of time, over plywood and sod, for different release rates, are very good; there is some scatter in the experimental findings but this is expected.

The information in Table 1 indicates the comparison of physical and mathematical results for maximum depth, are very good for plywood. The comparisons for the sod experiments are not particularly good but it must be noted that the mathematical model as developed to date does not include infiltration and/or evaporation. Infiltration was significant in the tests conducted on sod thus resulting in the smaller measured depths reported in Table 1. The mathematical model will be extended in the near future to include these additional concerns.

CONCLUSIONS

Preliminary findings indicate a good comparison between physical and mathematical model results. The results of the physical model being collected in this study will provide useful base data for both this study and other future work. As well, the success of the mathematical model while retaining a very simple structure indicates that it will be useful to address many interesting questions related to spills of liquids on soils.

ACKNOWLEDGEMENTS

The research is being funded by the Environmental Emergencies Technology Division (EETD) of Environment Canada, Dr. Mervin Fingas as Scientific Authority.

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TABLE I COMPARISON OF MAXIMUM DEPTHS

Surface Condition	Spill Rate (l/min)	Maximum Depths (mm) Measured*	Predicted
Plywood	21	9, 10	7
	77	11, 12	11.9
Sod	21	25	39
	77	37, 45, 33	72

* as determined from replicated experiments

FIGURE 1 SCHEMATIC OF SPILL PROCESS AND CHARACTERISTICS

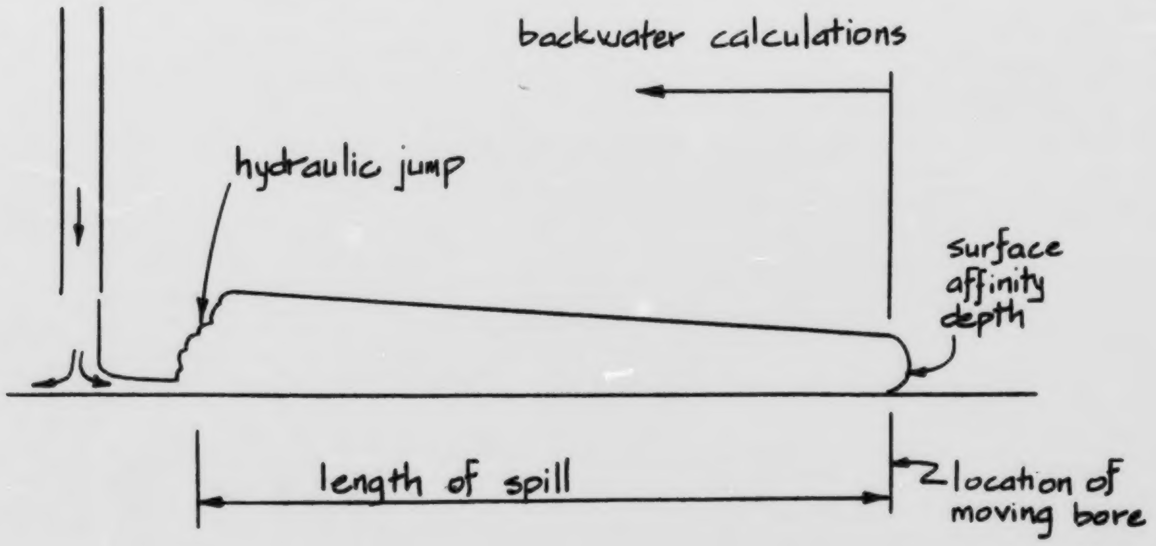

backwater calculations
hydraulic jump
surface affinity depth
length of spill
location of moving bore

FIGURE 2 2-DIMENSIONAL TEST BED

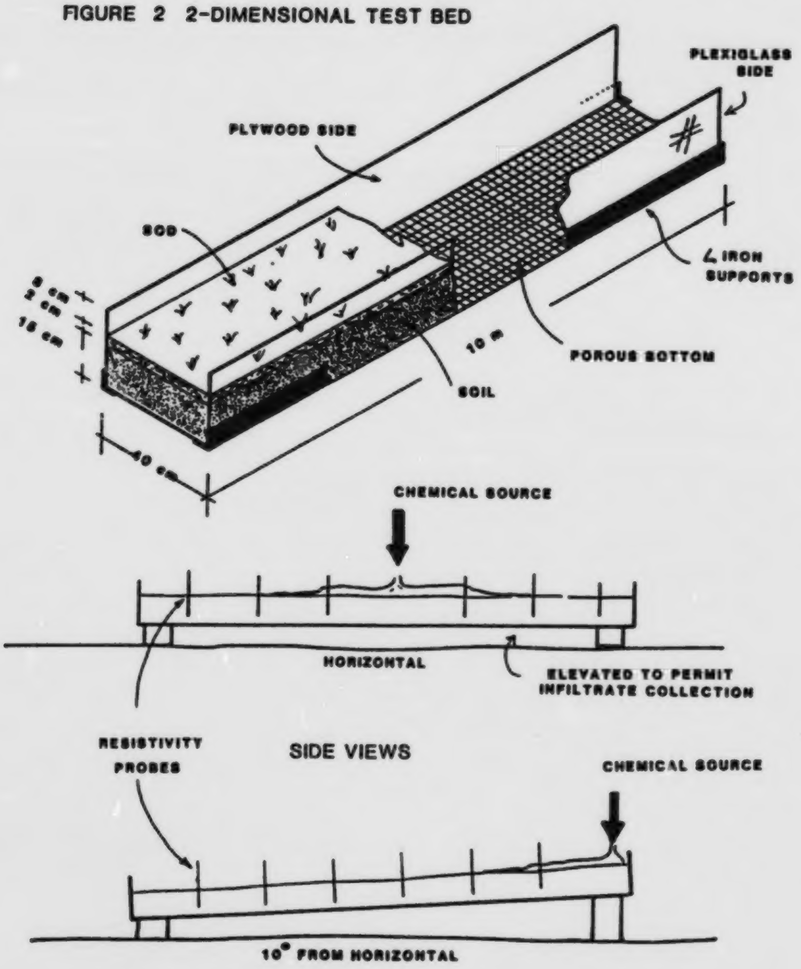
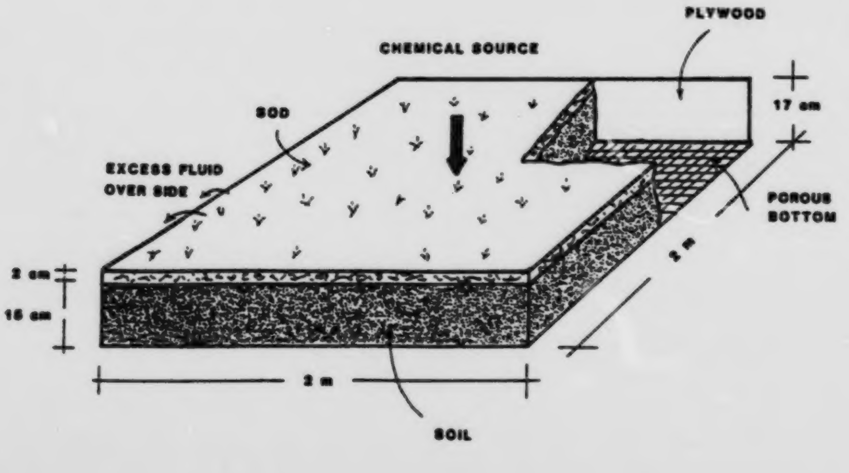

PLEXIGLASS SIDE
PLYWOOD SIDE
SOD
∠ IRON SUPPORTS
8 cm
2 cm
15 cm
10 m
POROUS BOTTOM
SOIL
40 cm
CHEMICAL SOURCE
HORIZONTAL
ELEVATED TO PERMIT INFILTRATE COLLECTION
RESISTIVITY PROBES
SIDE VIEWS
CHEMICAL SOURCE
10° FROM HORIZONTAL

FIGURE 3 3-DIMENSIONAL TEST BED


PLYWOOD
CHEMICAL SOURCE
SOD
17 cm
EXCESS FLUID OVER SIDE
POROUS BOTTOM
2 cm
15 cm
2 m
2 m
SOIL

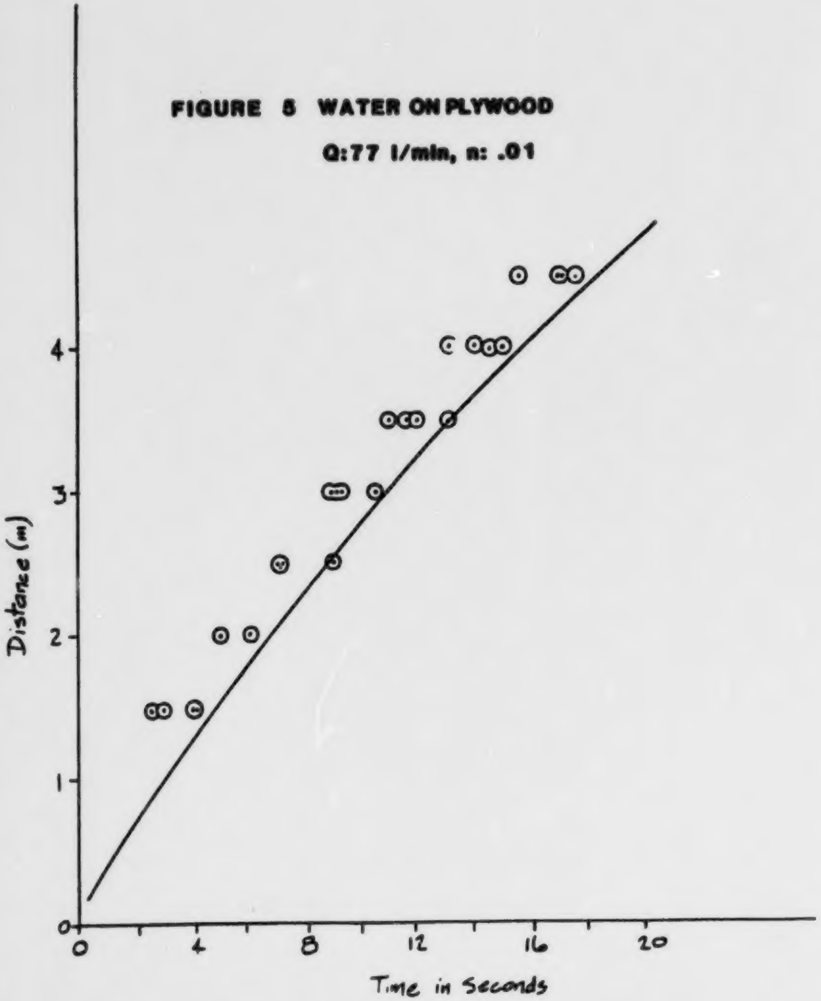


FIGURE 5 WATER ON PLYWOOD

Q:77 l/min, n: .01

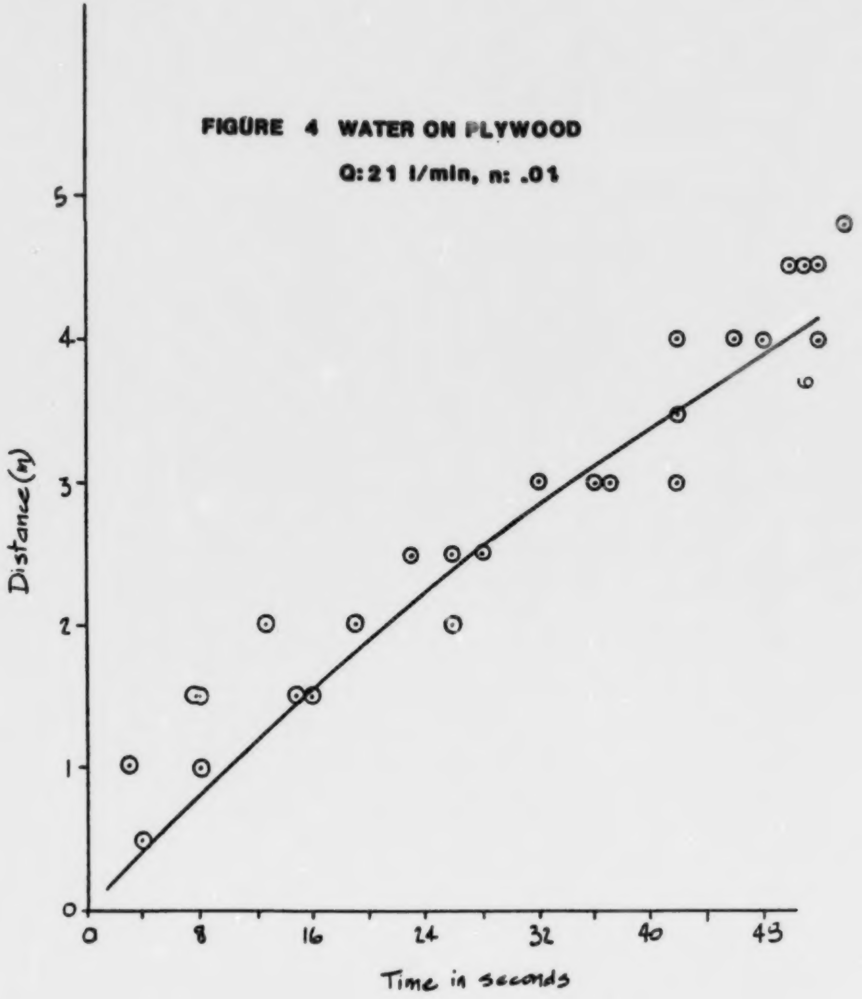


FIGURE 4 WATER ON PLYWOOD

Q:21 l/min, n: .01

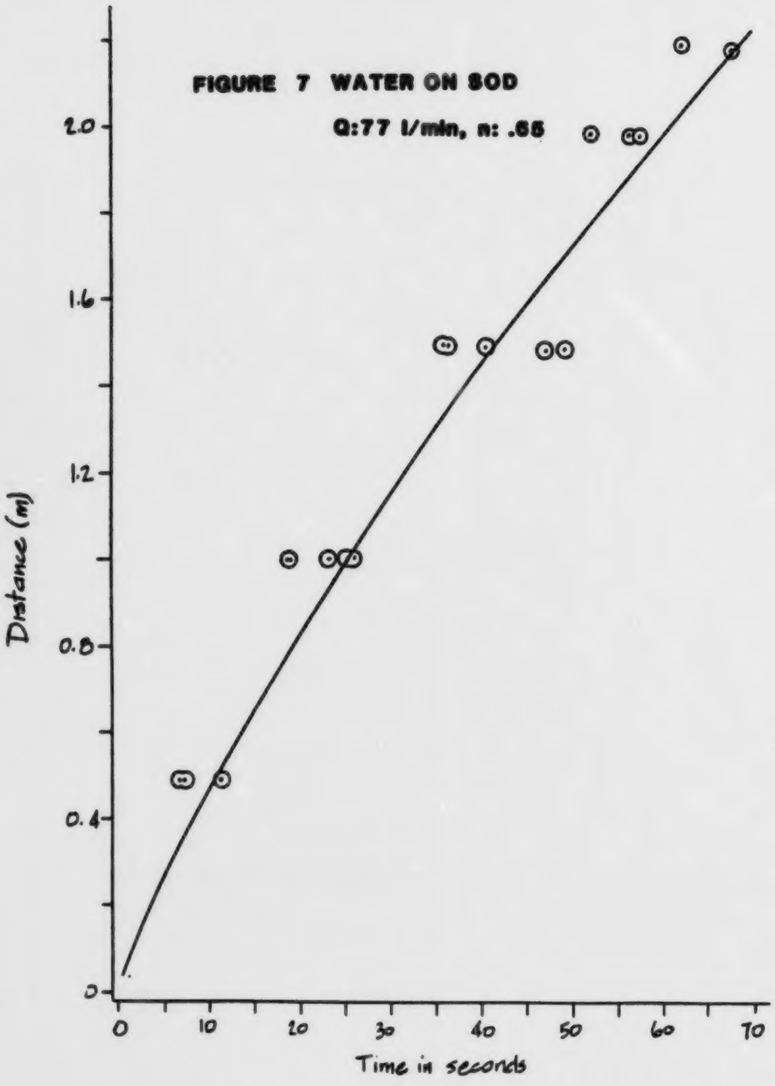


FIGURE 7 WATER ON SOD

Q:77 l/min, n: .65

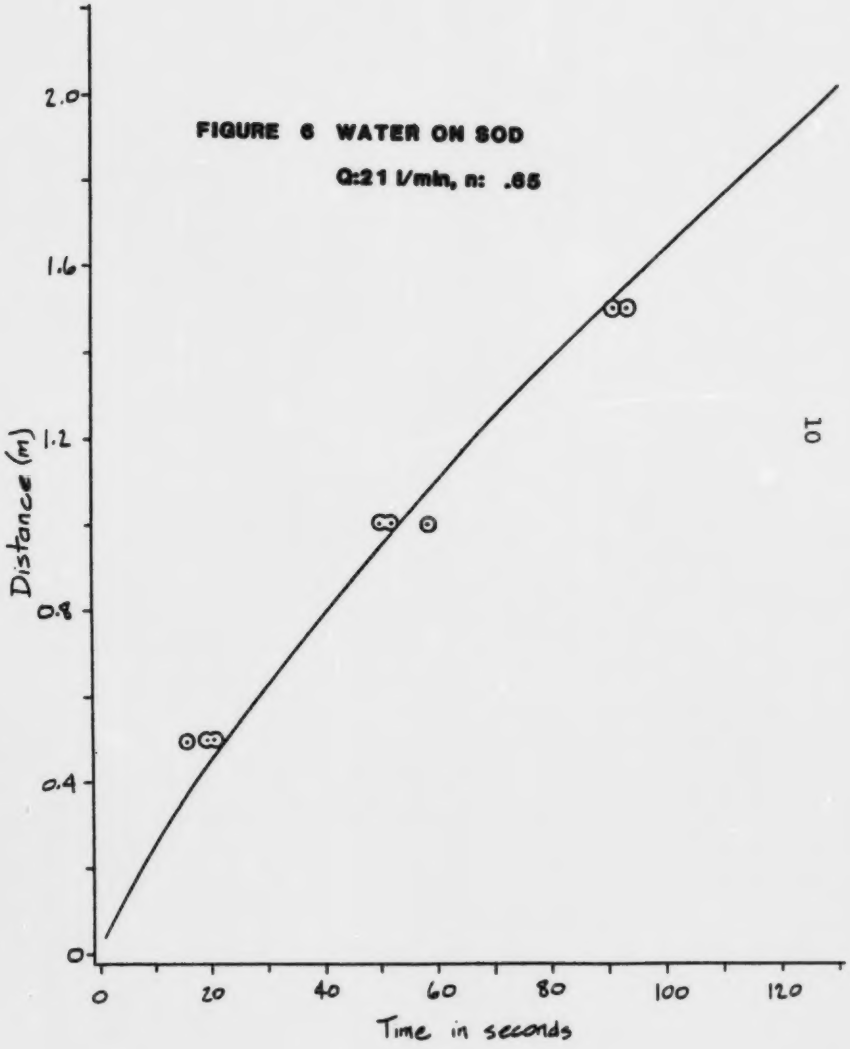


FIGURE 6 WATER ON SOD

Q:21 l/min, n: .65

SUBSURFACE CONTAMINATION FROM SPILLS OF DENSE NON-AQUEOUS PHASE LIQUID (DNAPL) CHEMICALS

Stan Feenstra

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ABSTRACT

Substances such as many halogenated solvents and PCBs comprise a group of organic chemicals which, in their pure form, can be categorized as dense non-aqueous phase liquid (DNAPL) chemicals. Approximately one quarter of the organic chemicals on the US EPA List of Priority Pollutants are DNAPL chemicals at typical subsurface temperatures. DNAPL chemicals are analogous to petroleum hydrocarbons in that they are immiscible in water, but DNAPL chemicals have densities which are greater than that of water.

The potential for subsurface contamination by DNAPL chemicals is significant because large quantities of such chemicals (especially chlorinated solvents) are used in many parts of our modern society, and the occurrence of spills during production, transportation and utilization is virtually inevitable. Although DNAPL chemicals are immiscible in water, their solubilities (typically 1 to 1000 mg/L) can often be many orders of magnitude higher than their respective drinking water standards. The combination of immiscibility and high density enables DNAPL at chemical spill sites to penetrate downward into the subsurface as a separate non-aqueous phase through both the vadose (unsaturated) zone and the groundwater zone below the water table. The tendency for DNAPL chemicals to sink through the groundwater zone differs from that of petroleum hydrocarbons which will float on the groundwater zone due to their lower density. In the subsurface, small but significant quantities of chemicals can be dissolved by the groundwater in contact with the DNAPL and can result in groundwater contamination.

The presence of DNAPL chemicals in the subsurface in the form of residual concentrations retained on the soil or as pools of pure product will have very significant implications with regard to the control of groundwater contamination at chemical spill sites. DNAPL chemicals can potentially penetrate downward into the subsurface to beyond the depth of feasible removal by excavation. Conventional methods for the removal of contaminated groundwater or floating non-aqueous phase liquids (ie. petroleum) such as purge wells and collector trenches may not be effective for the removal of DNAPL because DNAPL movement is not strictly controlled by groundwater flow. Because DNAPL chemicals remaining in the subsurface at the site of a chemical spill can continue to be a significant source of groundwater contamination, novel methods for the removal of DNAPL chemicals from the subsurface must be developed.

INTRODUCTION

Substances such as many halogenated aliphatic hydrocarbons, halogenated benzenes, phthalate esters and polychlorinated biphenyls (PCBs) comprise a group of organic chemicals which in their pure form can be categorized as dense non-aqueous phase liquid (DNAPL) chemicals. DNAPL chemicals are analogous to petroleum hydrocarbons in that they are immiscible in water, but unlike petroleum hydrocarbons, DNAPL chemicals have densities which are greater than that of water. Approximately one quarter of the organic chemicals on the U.S. EPA List of Priority Pollutants are DNAPL chemicals at typical subsurface temperatures (See Table 1).

In addition to the chemicals which in their pure form comprise DNAPLs, mixtures of chemicals can also comprise DNAPLs. For example, coal tar creosote is a complex mixture of polycyclic aromatic hydrocarbons (PAH) such as naphthalene, anthracene and phenanthrene, and various phenols and methylated phenols. The individual PAH compounds are solids at typical subsurface temperatures and the phenols are less dense than water, but the creosote mixture has DNAPL characteristics.

TABLE 1. U.S. EPA Priority Pollutants which are DNAPL chemicals at typical subsurface temperatures.

Methylene chloride
Chloroform
Carbon tetrachloride
1,2-Dichloroethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
1,1-Dichloroethylene
Trans-1,2-Dichloroethylene
Trichloroethylene
Tetrachloroethylene
1,2-Dichloropropane
Hexachlorobutadiene
Hexachlorocyclopentadiene
Bromodichloromethane
Bromoform
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,2,4-Trichlorobenzene
Nitrobenzene
Diethyl phthalate
Di-n-butyl phthalate
Polychlorinated biphenyls

The potential for groundwater contamination by DNAPL chemicals is significant because very large quantities of the chemicals are produced, transported and used in many parts of society, low levels of contamination can be of concern, and small quantities can potentially result in serious groundwater contamination problems.Table 2 shows the 1984 U.S. production of selected organics chemicals which can be categorized as DNAPL chemicals. Production quantities range up to several billion kilograms per year.

TABLE 2. 1984 U.S. production of selected organic chemicals which can be categorized as DNAPL chemicals.

	(10^6 lb.)	(10^6 kg)
Dichloroethylene	15,650	7,100
Carbon tetrachloride	730	330
1,1,1-Trichloroethane	710	320
Tetrachoroethylene	615	280
Methylene chloride	580	260
Chloroform	430	200

From American Chemical Society (1985).

Although DNAPL chemicals are immiscible in water and have relatively low solubilities in water (typically tens to several thousand milligrams per litre), their solubilities can often be many orders of magnitude higher than their respective drinking water standards (See Table 3).

TABLE 3. Solublity of selected DNAPL chemicals compared to typical drinking water standards.

Chemical	Solubility in Water (mg/L)	New York State Drinking Water Standard (mg/L)
Trichloroethylene	1100	0.01
Chloroform	8200	0.1
Carbon tetrachloride	785	0.005
PCB	0.012-0.15	0.0001

Drinking water standards are low because dissolved concentrations of tens to several hundred micrograms per litre in groundwater used for water supply can result in taste and odour problems and are considered to represent potential health risks. Because drinking water standards for many DNAPL chemicals are so low, small quantities can result in large-scale groundwater contamination problems. For example, 7 L or 10 kg of trichloroethylene could potentially contaminate 10^8 L of groundwater to a concentration of 0.1 mg/L or 10 times the New York State drinking water standard. In a sand aquifer, this volume of contaminated ground water would represent a plume 50 m in width, 10 m in depth, and 670 m in length.

The potential for groundwater contamination by DNAPL chemicals is also significant because of their distinctive physical and chemical properties. As previously noted, DNAPL chemicals are immiscible in water and have densities greater than water and, in addition, many have viscosities less than water (See Table 4).

The combination of low solubility, high density and frequently low viscosity can enable DNAPL from chemical spill sites to penetrate downward into the subsurface through the unsaturated and/or saturated zones as a separate non-aqueous phase. The tendency for DNAPL chemicals to sink through the saturated zone differs from that of petroleum hydrocarbons which will float on the groundwater in the saturated zone due to their lower densities. In the subsurface, small but significant quantities of chemicals can be dissolved by groundwater in contact with the DNAPL and can result in groundwater contamination.

TABLE 4. Physical and chemical properties of selected DNAPL chemicals.

Chemical	Solubility (mg/L)	Density (g/cm^3)	Viscosity (centipoise)
Trichloroethylene	1100	1.47	0.57
Chloroform	8200	1.50	0.60
Carbon tetrachloride	785	1.58	0.97
1,4-Dichlorobenzene	79	1.24	0.72
1,1,2-Trichloroethane	4500	1.44	0.12
Bromoform	3100	2.90	2.15
Gasoline	150-300	0.7-0.8	0.5-0.7
Crude Oil	5-25	0.8-0.9	3-35
Water	-	1.00	1.12

All properties at approximately 20°C.
Solubility data for chemicals from Callahan et al. (1979), density and viscosity data for chemicals from Dean (1979), data for petroleum products from Schwille (1981).

CASES OF GROUNDWATER CONTAMINATION BY DNAPL CHEMICALS

The principal documented occurrences of groundwater contamination by DNAPL chemicals have resulted from leaks or spills of chemicals from manufacturing facilities and from leakage from chemical waste disposal facilities. Coal tar creosote, a mixture of polycyclic aromatic hydrocarbons, phenol and methylated phenols, was found to have resulted in groundwater contamination at wood preservative plants in Minnesota and New York (Ehrlich et al., 1982; Burgess et al., 1984). In both cases, creosote (typical density 1.5 g/cm^3) from spills and waste disposal activities was found to have penetrated into sand or sand and gravel strata both above and below the water table. Askarel, a mixture of polychlorinated biphenyls (PCBs) and trichlorobenzene, was found to have resulted in groundwater contamination at an electrical transformer manufacturing plant in Saskatchewan (Schwartz et al., 1982). In this case, the askarel (density of 1.5 g/cm^3) penetrated into fissured silts and clays both above and below the water table. Groundwater contamination from DNAPL chemicals has occurred at several chemical waste disposal facilities in the Niagara Falls area of New York State. At the Hyde Park and S-Area disposal sites, mixtures of organic chemicals (estimated density 1.5 g/cm^3) have penetrated into the subsurface through fissured dolostone bedrock (Guswa and Faust, 1984; Clarke and Kay, 1984). All these examples represent cases in which the DNAPL chemicals were introduced into the subsurface from either a well defined source (ie. a chemical spill) and/or in very large quantities (ie. thousands of litres).

In situations where the quantities of DNAPL are smaller or originates from a poorly defined source (such as a slow continuing leak from an underground tank or line), it may not be possible to reliably identify the presence of DNAPL in the subsurface. For example, a spill of approximately 800 L of DNAPL could potentially be contained in a volume of sandy soil measuring 3.0 m by 3.0 m by 0.3 m. Such a quantity of DNAPL could comprise an extremely significant source of groundwater contamination but a pool of DNAPL of this size would not likely be detected given the borehole spacings for typical hydrogeological investigations.

GROUNDWATER CONTAMINATION BY DNAPL CHEMICALS

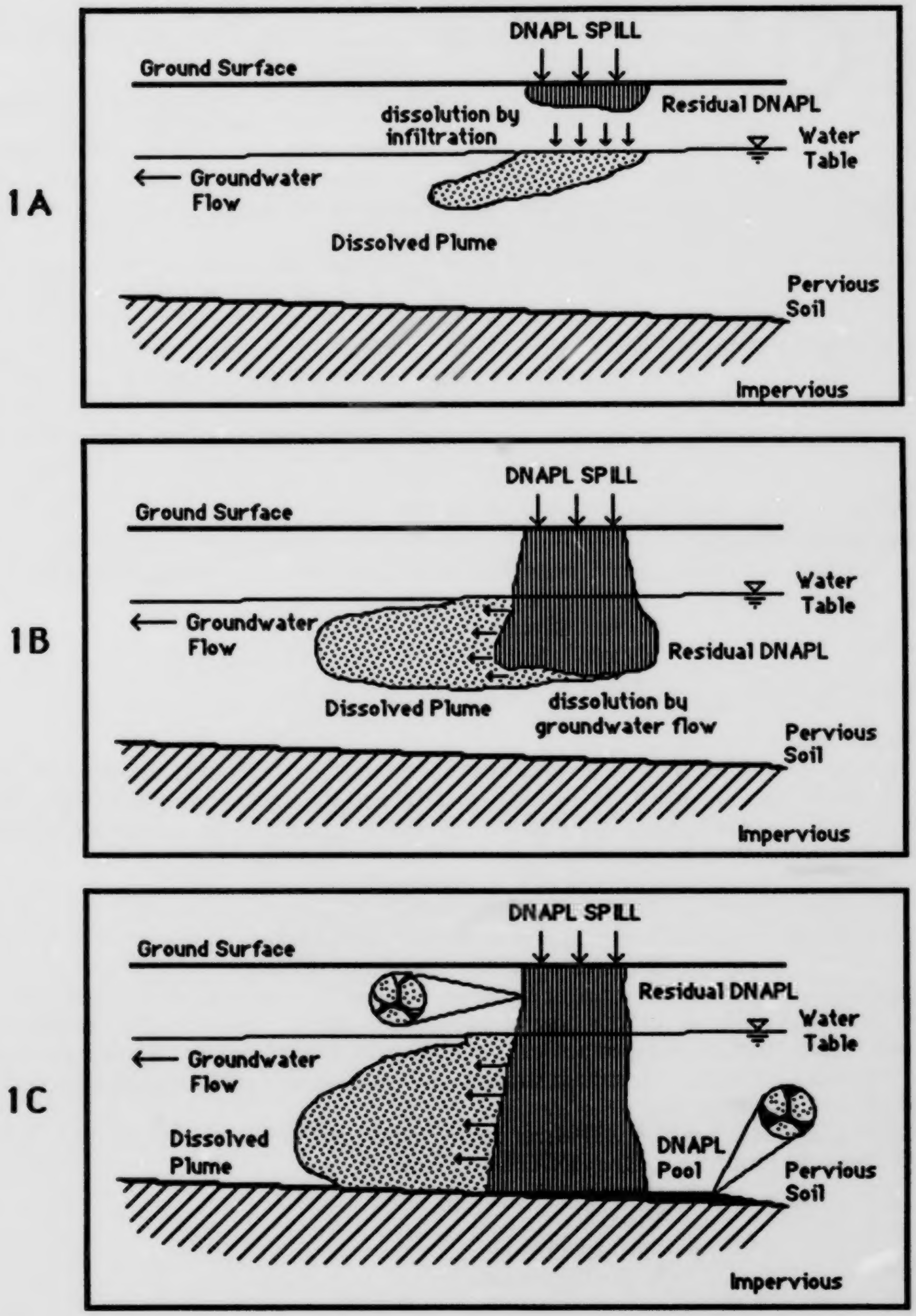
It is evident from the preceding examples that DNAPL chemicals have resulted in very significant subsurface contamination problems at many sites and may be important, but yet unrecognized, sources of contamination at other sites. However, there have been few studies which have considered in detail the movement of such chemicals in the subsurface and the development of groundwater contamination from such sources. Consequently these processes are not adequately understood.

Pioneering research into DNAPL chemicals in the subsurface was conducted starting in the mid-1970's by Friedrich Schwille at the Federal Institute of Hydrology in Koblenz, Federal Republic of Germany. Schwille's work has primarily involved small-scale and large-scale laboratory simulations of DNAPL penetration into unsaturated and saturated granular geologic materials. Unfortunately most of this research has never been published in English and is largely unknown in North America. Two English summary papers describing the conceptualization and laboratory simulation of DNAPL movement in the subsurface are Schwille (1981) and Schwille (1984).

Based on the pioneering work of Schwille and observations at a variety of chemcial spill and waste disposal sites in North America three general conceptualizations for the development of groundwater contamination in sandy aquifers can be described and are shown in Figure 1. In these conceptualizations, a quantity of DNAPL chemical is introduced into the aquifer such as might occur due to a chemical spill. In such situations, DNAPL could penetrate downward through the unsaturated zone and the saturated zone due to its high density. In case A, all of the DNAPL forms a residual in the unsaturated (vadose) zone because the input volume does not exceed the retention capacity of the vadose zone. Within this residual zone the DNAPL is present as immobile unconnected and partially connected blobs and filaments. The few data available on residual contents of DNAPL chemicals in soils indicate DNAPL contents of 30 to 50 L/m^3 or 10 to 30% of the pore space in sandy soils (Schwille, 1984; F. Schwille, personal communication). Such residual contents are comparable to the residual contents typically observed for petroleum hydrocarbons (Wilson and Conrad, 1984). Groundwater contamination develops when water that infiltrates through the residual zone carries dissolved DNAPL-derived contaminants to the water table. As infiltration of precipitation occurs from time to time, a plume of dissolved contaminants develops in the groundwater zone.

In case B, the input volume of DNAPL is sufficiently large for excess DNAPL to move into the groundwater zone but not large enough for an excess to reach the bottom of the aquifer. Dissolved contaminants derived from the residual DNAPL in the vadose zone and residual DNAPL in the groundwater zone cause a contaminant plume to develop.

Figure 1. Subsurface Contamination by DNAPL Chemicals.


1A
DNAPL SPILL
Ground Surface
Residual DNAPL
dissolution by infiltration
Water Table
Groundwater Flow
Dissolved Plume
Pervious Soil
Impervious
1B
DNAPL SPILL
Ground Surface
Water Table
Groundwater Flow
Residual DNAPL
Dissolved Plume
dissolution by groundwater flow
Pervious Soil
Impervious
1C
DNAPL SPILL
Ground Surface
Residual DNAPL
Water Table
Groundwater Flow
Dissolved Plume
DNAPL Pool
Pervious Soil
Impervious

If the volume of spilled DNAPL is larger than the retention capacity of the vadose and groundwater zones, a portion of the DNAPL will settle out as a pool of free liquid on the bottom of the aquifer as shown in case C, or it will settle out on the first low permeability bed in the aquifer. In each of these conceptualizations, groundwater in the aquifer acquires dissolved chemicals from the DNAPL residual, or in case C, from the residual and the pool on the bottom of the aquifer. In situations where the confining stratum is sloped, DNAPL can continue to move downslope and its movement need not be controlled by the direction of groundwater flow.

Many of the dissolved industrial solvents are not strongly influenced by adsorption on aquifers solids and are not rapidly removed by biodegradation. Therefore, in each of these conceptualizations, large plumes of groundwater contamination can develop as groundwater flow carries the dissolved compounds away from the site. The dissolution of DNAPL from the residual zones and DNAPL pools will continue and a plume of contaminated groundwater will be generated so long as DNAPL remains in the subsurface.

The potential importance of such a DNAPL source cannot be overstated. For example, consider a hypothetical case of a trichloroethylene (TCE) spill on sandy soil which results in a residual zone measuring 6 m by 6 m in area and 3 m in depth with a residual TCE content of 30 L/m^3 (2.4 weight percent or 24000 mg/kg). Such a residual zone could contain approximately 3200 L or 4800 kg of TCE. Similarly a small pool of TCE measuring 6 m by 6 m in area and 0.2 m in thickness in a sandy soil could contain approximately 2200 L or 3300 kg of TCE. These are very significant quantities in relation to typical drinking water standards for TCE of several micrograms per litre.

FACTORS INFLUENCING SUBSURFACE CONTAMINATION BY DNAPL CHEMICALS

The factors which will influence the nature and extent of contamination resulting from the presence of DNAPL in the subsurface can be categorized as:

-Factors affecting DNAPL migration
-Factors affecting dissolution of DNAPL and transfer to the groundwater

DNAPL Migration

There are a variety of factors which will affect the migration of DNAPL chemicals in the subsurface. These factors include both chemical-specific and site-specific considerations. The primary factors which can affect the migration of DNAPL chemicals in the subsurface relate to the nature of the chemical source and include:

-The type of DNAPL chemicals
-The volume of chemicals spilled
-The time period over which the spill(s) occurred
-The area of infiltration of the chemicals

In the case of significant single incident chemical leaks and spills, suitable information on these factors may be available. However, this type of information may not be avalilable for cases where contamination results from slow continual leaks such as may occur from an underground storage tank or line, or from numerous intermittant smaller spills such as can occur around chemical loading and off-loading areas.

Chemical-specific factors which will affect the migration of DNAPL chemicals relate to the physical and chemical properties of the DNAPL and include:

-Density
-Viscosity
-Surface tension
-Vapour pressure

The density and viscosity of the DNAPL are the principal factors which will control the relative mobility of the DNAPL. DNAPL chemicals can move at a different rate than water through a given geologic medium. For DNAPL saturated conditions, the relative permeability of the DNAPL, k_{DNAPL} is related to the intrinsic permeability of the medium, k by:

$$k_{DNAPL}=\frac{\rho k}{\mu}$$

where ρ is the density of the DNAPL and μ is the kinematic viscosity of the DNAPL. Many DNAPL chemicals have densities significantly higher than that of water and viscosities lower than that of water (see Table 4). Consequently these chemicals can have a relative permability higher than that of water and can potentially move through the subsurface more readily than water.

The surface tension or interfacial tension between the DNAPL and the water, air and solid phases in the subsurface will affect the capillary pressures acting on the DNAPL. Capillary effects will determine the degree of retention of DNAPL on geologic materials (ie. the residual DNAPL content) and can also restrict the movement of DNAPL from coarse-grained soils into finer grained soils. DNAPL chemicals having low interfacial tensions will be retained to a lesser degree (ie. lower residual content) on a given geologic material compared to DNAPL chemicals having higher interfacial tensions. Numerical computer simulations by Guswa and Faust (1984) indicate that capillary pressure relationships can be sufficient to prevent downward migration of DNAPL through fine-grained soils even under conditions where there are downward hydraulic gradients. The movement of DNAPL chemicals into fine-grained soils will be restricted by capillary pressures to a lesser degree for DNAPL chemicals having low interfacial tensions, compared to those chemicals having higher interfacial tensions.

The vapour pressure of DNAPL chemicals can also affect the migration of DNAPL in the subsurface. DNAPL may be lost from the shallow unsaturated zone by volatilization of high vapour pressure compounds to the atmosphere. Such losses of mass will act to restrict further downward migration if the losses are significant.

Data on the properties such as density, viscosity, interfacial tension and vapour pressure are available for most DNAPL chemicals at 20-25°C. Data on these properties at temperature representative of most subsurface conditions (5-10°C) are generally limited. Similarly, data on these properties for mixtures of chemicals are not generally available, and these data may considerably different than those for the individual component chemicals. In particular, by analogy with petroleum hydrocarbons, the interfacial tension of DNAPL chemicals is expected to vary significantly with changes in the pH and chemical composition of the groundwater. However, these effects have not been documented.

Site-specific factors which will affect the migration of DNAPL chemicals relate to the properties of the geologic materials and include:

-stratigraphy
-intrinsic permeability
-relative DNAPL permeability
-groundwater flow pattern

Stratigraphy and intrinsic permeability will have significant effects on the migration of DNAPL. All other factors being equal, DNAPL will move more readily through high permeability strata such as sands while movement will be restricted in low permeability strata such as clays. The relative permeability of DNAPL in geologic media will be a function of the intrinsic permeability, the properties of the DNAPL (density, viscosity, interfacial tension), the nature of the voids, and the proportion of the voids filled by DNAPL, air and water. The highest DNAPL permeability occurs when the voids are completely filled by DNAPL. At increasing air or water contents, the DNAPL permeability is reduced. The relative permeability of petroleum hydrocarbons (oil), as a function of the air and water content, has been determined experimentally and is well documented. The relative permeability relations for DNAPL chemicals are likely to be analogous in form to those of petroleum hydrocarbons but may be very different in value because many DNAPL chemicals have viscosities and interfacial tensions considerably different than those of petroleum hydrocarbons.There are no published data available which illustrate the relative permeability of DNAPL chemicals with these characteristics.

Groundwater flow patterns can also affect the migration of DNAPL chemicals in the subsurface although DNAPL migration will not be strictly controlled by groundwater flow. Particularly, upward groundwater flow may prevent further downward movement of DNAPL through the groundwater zone. Numerical computer simulations by Guswa and Faust (1984) have illustrated that an upward groundwater gradient can prevent downward DNAPL migration.

Significant efforts have been directed at the development of computer models for the simulation and ultimate prediction of DNAPL migration through the subsurface. A variety of one- and two-dimensional, two-phase (DNAPL-water or DNAPL-air) and three-phase (DNAPL, air and water) models have been developed by Guswa and Faust (1984), Farquhar and McBean (1985) and Abriola and Pinder (1985) to simulate the penetration of DNAPL chemical into the subsurface from a surface spill. Although these models incorporate the principal controlling parameters into their formulation, they are at present limited by the lack of actual input values for many of the key parameters such as relative permeability.

Dissolution of DNAPL and Transfer to Groundwater

At the present time, there are virtually no quantitative data regarding the dissolution rate or factors controlling the dissolution of DNAPL chemicals in the subsurface. However, conceptually there are several factors which will affect the dissolution of DNAPL chemicals and the transfer of dissolved chemicals to the groundwater. A key factor which will affect the dissolution of DNAPL is the distribution of DNAPL in the subsurface in relation to the groundwater flow pattern. For example, although there is no documented evidence in this regard, the dissolution of DNAPL and transfer to the groundwater may be more effective as groundwater sweeps through a zone of residual DNAPL compared to when groundwater sweeps across the top of a DNAPL pool at the bottom of an aquifer. In the zone of residual DNAPL, there may be a much larger surface area of DNAPL-groundwater contact and dissolution will be more effective. Conversely, the presence of DNAPL as a residual filling a portion of the pore space may be sufficient to reduce the permeability of water through the residual zone and dissolution of the DNAPL may be inhibited.

The dissolution of DNAPL chemicals will also depend on the solubility of the chemicals in water. As shown in Table 2, the solubility of various DNAPL chemicals can vary by several orders of magnitude. Data on the solubility of various DNAPL chemicals in distilled water are generally available but data on the water solubilities of individual components in chemical mixtures are limited. The solubilities of individual petroleum hydrocarbons can be significantly increased or decreased by the presence of other hydrocarbons (Kebe et al., 1983) and, by analogy, the behaviour of DNAPL chemicals may be comparable. Small-scale laboratory experiments (Pfannkuch, 1984; F. Schwille, personal communication) have shown that the pore water in contact with DNAPL quickly acquires dissolved chemicals at concentrations approaching the theoretical solubility of the DNAPL chemical. This condition is, however, seldom observed in field spill situations where maximum dissolved concentrations in the groundwater are typically only several percent of the theoretical solubility concentration. This phenomenon is likely the result of heterogeneous distribution of DNAPL in the subsurface, the non-uniform pattern of groundwater flow in and around the DNAPL residual zones and pools, and the tendency for a mixing or blending of groundwater from various depths during sample collection from monitoring wells.

A thorough evaluation of the factors controlling the dissolution of petroleum hydrocarbons in the subsurface was conducted by Pfannkuch (1984). The same factors controlling petroleum dissolution are likely to be applicable to the dissolution of DNAPL chemicals in the subsurface.

Conceptually, the source strength of a DNAPL zone or pool, *S* , or mass transfer per unit time is related to an exchange constant, *E* , and the contact area, A_c between the DNAPL and the groundwater by:

$$S = EA_c$$

Unfortunately the parameters E and A_c are not precisely defined and cannot yet be determined for DNAPL in porous media. Laboratory experiments conducted during the 1970's by researchers in Europe were contradictory. One set of experiments determined that *E* and consequently the source strength *S* was diffusion-controlled and independent of the groundwater velocity, while other experiments determined that *E* was dependent on the groundwater velocities. These experiments were re-evaluated by Pfannkuch (1984) who now considers that at low groundwater flow velocities the mass transfer of dissolved contaminants to the groundwater is diffusion-controlled and not dependent on the groundwater velocity. At higher groundwater velocities the mass transfer becomes dependent on the groundwater velocity and becomes controlled by the solubility of the DNAPL.

CONCLUSIONS: IMPLICATIONS OF DNAPL CHEMICALS IN THE SUBSURFACE

The presence of DNAPL chemicals in the subsurface has significant implications regarding the interpretation of groundwater contamination patterns and the design of remedial measures at chemical spill sites. The penetration of DNAPL into the subsurface extends the source of groundwater contamination from at or close to the ground surface to a potentially far greater depth. This means that groundwater contamination patterns resulting from a DNAPL source may be significantly different than that which might develop from a near-surface source.

The presence of a DNAPL source may result in the highest concentrations of dissolved chemcials occurring at the base of an aquifer rather than near the top as would be typical of a near-surface contamination source. Therefore, the possible presence of a deeper DNAPL source should be considered in the planning of borehole and monitoring well locations and depths for hydrogeologic investigations at chemical spill sites.

The existence of DNAPL chemicals in the subsurface will also have implications with regard to remedial measures to control groundwater contamination at chemical spill sites. DNAPL chemicals can potentially penetrate downward into the subsurface to beyond the depth of feasible removal by excavation. Similarly, DNAPL chemicals can also migrate into areas which are otherwise inaccessible such as beneath buildings or process areas. These zones of residual DNAPL and DNAPL pools can comprise very significant sources of long-term groundwater contamination unless they are removed. Simply purging and treating contaminated groundwater from the dissolved plume will not generally be effective in remediating the contaminant source because the residual zones and pools can represent such a large mass of chemical. Long-term solution of the groundwater contamination problem must be directed at removal of the source.

Conventional methods for the removal of contaminated groundwater or floating non-aqueous phase liquids (ie. petroleum) such as purge wells and collector trenches may not be effective for the removal of DNAPL because the movement of DNAPL is not strictly controlled by the groundwater flow pattern. DNAPL pools cannot be reliably recovered by hydraulic means. Recovery wells installed directly within a DNAPL pool can be used to recover some quantity of pure chemical but the radius of influence of such wells is small and the DNAPL pools can be difficult to locate precisely. The DNAPL in the residual zone is, by its very nature, immobile under the ambient potentiometric conditions.

At the present time, excavation and removal of the contaminated soil is the only method which has been demonstrated to be an effective means of remediating DNAPL chemical spill areas.

In areas where DNAPL chemicals have penetrated beyond the depth of feasible removal by excavation or exist in otherwise inaccessible locations, the remediation of the residual zones and pools may only be possible by novel in situ removal techniques.
Possible options for in situ removal methods can include:

1. Induced Volatilization
   The removal of volatile DNAPL chemicals from residual zones and pools above the water table may be possible using induced volatilization methods. Such methods would involve increasing the rate of advective gas flow through the soil. This would likely be accomplished by means of a system of pressurized wells to force air into the soil with vacuum wells to remove the air and volatile chemicals released to the soil gas from the DNAPL. The effective removal of gasoline from soil by induced volatilization has been demonstrated using laboratory and small field-scale experiments by Marley and Hoag (1984) and Thornton and Wootan (1982).

2. Hydraulic Removal
   The removal of DNAPL from residual zones above or below the water table may be possible using hydraulic methods to increase the rate of groundwater flow sufficiently through the residual zone to physically displace the blobs and filaments of DNAPL. Increased groundwater flow would likely be effected by a system of injection wells and purge wells.This method has been evaluated by Wilson and Conrad (1984) who concluded that hydraulic removal of residual petroleum would be possible in hydrogeologic environments in which sufficiently large hydraulic gradients can be established.

3. Chemically-enhanced Hydraulic Removal
   Hydraulic removal of residual DNAPL from above or below the water table as described above may be enhanced by the addition of surfactants or other chemical agents which will reduce interfacial tensions of the DNAPL and allow the chemical to be more readily displaced by flowing groundwater. Such techniques are frequently used for the enhanced recovery of crude oil in petroleum production.

4. Accelerated Dissolution
   The removal of DNAPL from residual zones and pools above or below the water table may be possible using methods to increase the rate of groundwater flow through the contaminated zones and intentionally dissolve the DNAPL. As with the hydraulic removal methods, the increased groundwater flow would likely be effected by a system of injection wells and purge wells. The key uncertainty in such a removal method is the dependency of the DNAPL dissolution rate on the groundwater flow velocity. If DNAPL dissolution is primarily diffusion controlled, accelerated dissolution methods may be fruitless.

5. Chemically-enhanced Dissolution
   Accelerated dissolution methods for the removal of DNAPL from residual zones and pools may be enhanced by the addition of miscible co-solvents to the groundwater to increase the solubility of DNAPL in the groundwater swept through the residual zones or across the DNAPL pools. This type of method may be particularly effective in the removal of DNAPL pools compared to the previously described methods.

The first three of these possible remediation options are based on techniques which have already evaluated or used for the recovery of petroleum products from the subsurface, but have not been demonstrated to be applicable to the remediation of DNAPL chemicals. The remaining remedial options are based only on a conceptual evaluation of DNAPL removal. Further research is required to evaluate and demonstrate the effectiveness of such remedial measures for the removal of DNAPL chemicals from the subsurface.

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HAZARD ASSESSMENT OF AQUATIC ORGANISMS EXPOSED TO CHEMICALS AFTER AN ACCIDENTAL SPILL FROM BULK TANKERS AT SEA

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SUMMARY

The influence of different physico-chemical properties of liquid organic chemicals on the exposure of aquatic organisms after an accidental spill from a bulk tanker at sea was evaluated.
On the basis of the results it is concluded that:

- exposure is mainly a function of vapour pressure, density and water solubility, and
- that very large differences can exist in exposure of marine organisms to different chemicals.

Based on the results a proposal is made for the classification of chemicals in three exposure categories. Integration of these exposure categories with existing aquatic toxicity ratings enables an environmentally realistic hazard rating.

1. INTRODUCTION

Many chemicals are transported in bulk by ship at sea. As a result of accidental spills or discharges of tank washings these chemicals may enter the marine environment and affect aquatic organisms. Both effects on the viability and on the taste of sea food organisms may occur. Because of the potential economic implications of these effects for the fisheries industry new legislation (e.g. MARPOL, 1973) is being developed to minimize the potential introduction into the sea of chemicals that pose a hazard in this respect.

So far, within the MARPOL framework and endorsed by the Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), only the inherent property of chemicals to cause toxic and/or tainting effects is taken into account for hazard ranking of these chemicals (1).

Hazard, by definition, is: "a function of toxicity (or tainting) and conditions of exposure which can result in an adverse biological effect". Thus, if ranking of chemicals should be based on their hazard towards living resources both toxicity (or tainting) and exposure should be taken into account. This is realistic since, if due to the characteristic fate and behaviour of a chemical the exposure of living resources is limited, the risk that adverse biological effects occur is also limited.

In this study a mathematical basis is developed for defining exposure condition for aquatic organisms in the marine environment after an accidental spill from a ship. The exposure conditions are defined as a function of the chemical's physico-chemical properties rather than as a function of varying spill and environmental conditions. To that purpose a set of organic chemicals is selected covering a broad range of physico-chemical properties.

The percentage of these chemicals that dissolves in water and the consequent water concentration is assessed for a limited number of different spill, and environmental conditions which are thought to be realistic, but concervative in a sense that the resulting assessment of the water concentrations represents a "worst-case" estimate. On basis of this assessment an exposure rating is developed which, together with a toxicity- or tainting-rating can be combined into a hazard rating.

2. SCOPE

The exposure of aquatic organisms to a chemical after an accidental spill at sea depends on the rate of the various fate processes that can occur. The rate of these processes depends on spill characteristics, environmental conditions and chemical properties. For the exposure assessment the following spill characteristics and environmental conditions, that were expected to be representative for real spills,were defined.

- Spill characteristics:
    - spill volume: 60 m^3 and 2000 m^3
    - release time: instantaneous and 24 hours
- Environmental conditions:
    - weather : calm and storm (wind speed about 10 and 30 $m.s^{-1}$)
    - water depth : 20 and 200 m
    - temperature : 10°C

Six liquid organic chemicals, having a density lower than that of sea water, were selected. Roughly these chemicals can be divided into the following groups, viz. chemicals having a:

- low water solubility and high vapour pressure : benzene and 1,4-xylene
- high water solubility and high vapour pressure: methyl ethylketone
- high water solubility and low vapour pressure : aniline, butanol and pyridine

The values of the relevant properties of these chemicals are given in Table 1.

Table 1. Chemical properties

Compound	Mol. W., $g.mol^{-1}$	Solubility (20-25°C), $mol.m^{-3}$	Vapour press. (20-25°C), bar	Boil. p., °C	Density (20°C) $kg.m^{-3}$
Benzene	78	22.8	$1.1x10^{-1}$	80	880
1,4-Xylene	106	1.87	$9.3x10^{-3}$	138	870
Methyl ethylketone	72	$4.90x10^{3}$	$1.0x10^{-1}$	80	805
Aniline	93	$3.66x10^{2}$	$4.0x10^{-4}$	184	1020
Butanol	74	$1.04x10^{3}$	$5.6x10^{-3}$	118	810
Pyridine	79	$5.71x10^{3}$	$1.9x10^{-2}$	115	982

3. FATE ASSESSMENT OF A CHEMICAL SPILL

The fate of a liquid organic chemical, having a relatively low water solubility, can be influenced by various processes during and after the spill. During the spill the chemical can be subjected to the jet mixing process. Subsequently, part of the chemical will form a floating layer on the sea surface or sink to the sea bottom depending on the density of the compound. In this study only the fate of chemicals that float on water is assessed. The fate of chemicals that sink is described in an other study (2).

The rate of the initial dilution and dissolution of a spilled compound caused by the jet mixing process depends on the jet flow and on the path length through the water. Generally the jet flow as well as the path length are far too small to cause a substantial dilution or dissolution. Thus, this process can be neglected and it can, therefore, be assumed that the bulk of the chemical initially will form a floating layer on the sea surface.

The floating layer of the chemical on the sea surface will be subjected to the processes spreading, evaporation, dissolution, and natural dispersion, which will occur simultaneously and thus influence each other (3,4). The rate and effects of these processes are estimated for an instantaneous spill and the implications for a spill with a release time of 24 hours are discussed.

3.1. Fate assessment of the floating layer

3.1.1. Spreading. Various models have been developed to describe the process of spreading of oil spilled at sea. Of these models that of Fay has been shown to give the most reliable results (4). We assumed this model to be applicable for spilled chemicals also (5).

The main physico-chemical parameters that are needed as inputs for Fay's model are the density and the net surface tension. The net surface tension, or spreading coefficient, is the difference between the air/water surface tension and the sum of the air/organic surface tension and the water/organic interfacial tension. For oil spreading coefficients have been found to be in the range of 20 to 25 $mN.m^{-1}$ or $dynes.cm^{-1}$ (4). For chemicals spreading coefficients have been found to be more variable. Data ranged from -13 $mN.m^{-1}$ for allyl chloride to 46 $mN.m^{-1}$ for butyl alcohol (5). For the chemicals, that are considered here, we assumed the value to be 25 $mN.m^{-1}$.Based on these physico-chemical parameters and on relevant properties of sea water, spreading of the chemicals can be calculated. The results indicate that for larger spills more time is needed to reach maximum spreading.

3.1.2. Evaporation Models for calculating the rate of evaporation and the amount of evaporated compound for oil floating on water have been discussed (4). The model developed by Mackay et al. has been found to be the most appropriate. In the absence of other verified models we have adapted this model for use for spilled chemicals.

The only physico-chemical parameter, that is needed as input for the model, is the distillation curve of the oil what property is closely related to the vapour pressure. For the pure chemicals, that are considered here, we assumed the distillation curve to range from its boiling point to its boiling point plus 1°C.

Obviously, the amount of evaporated compound depends also on the exposed surface area of the floating organic layer and thus on the rate of spreading. For the work described in ref. 4 an integrated computer program has been developed to calculate the amount of evaporated oil as a function of time taking into account the increasing surface area due to the process of

Table 2. Additive-volume increments for the calculation of molar volumes V_A

	Increment*, $m^3.mol^{-1} \times 10^6$
Carbon	14.8
Hydrogen	3.7
Oxygen (except as noted below)	7.4
In methyl esters and ethers	9.1
In ethyl esters and ethers	9.9
In higher esters and ethers	11.0
In acids	12.0
Joined to S,P,N	8.3
Nitrogen	
Doubly bonded	15.6
In primary amines	10.5
In secondary amines	12.0
Bromine	27
Chlorine	24.6
Fluorine	8.7
Iodine	37
Sulfur	25.6
Ring, three-membered	-6.0
Four-membered	-8.5
Five-membered	-11.5
Six-membered	-15.0
Naphthalene	-30.0
Anthracene	-47.5

* The additive-volume procedure should not be used for simple molecules. The following approximate values are employed in estimating diffusion coefficients for the simple molecules: H_2, 14.3; O_2, 25.6; N_2, 31.2, air, 29.9; CO, 30.7; CO_2, 34.0; SO_2, 44.8; NO, 23.6; N_2O, 36.4; NH_3, 25.8; H_2O, 18.9; H_2S, 32.9; COS, 51.5; Cl_2, 48.4; Br_2, 53.2; I_2, 71.5.

On basis of the results of the calculations described in section 3.1.2. the mass transfer flux of the compound into air was estimated using the equation:

$$F_g = \frac{V_s \rho}{A_a t_v} \qquad (4)$$

where: F_g is the average mass transfer flux into air ($kg.m^{-2}.s^{-1}$),
V_s is the spill volume (m^3),
ρ_s is the density of the compound ($kg.m^{-3}$),
A_a is the average surface area of the floating organic layer (m^2), and
t_v is the time after which the floating organic layer has evaporated totally (s).

As the organic surface layer disappears through evaporation as well as dissolution, it is obvious that the product of the real average surface area of the organic layer and the time after which the layer has been disappeared is smaller than calculated for evaporation only (equation 4). This product was calculated using equation 5:

It should be noted here that when the rate of evaporation is fast heat transport may become rate limiting for this process. This phenomenon was neglected in the calculations.

3.1.3. Dissolution The calculation of the concentration of a chemical in water as a result of the simultaneously occurring processes of spreading evaporation and dissolution requires an integrated computer program such as the program for calculating the combined effect of spreading of and evaporation from the organic surface layer. However, such a program is not as yet available and, therefore, calculations were simplified.

No experimental data were available on rates of dissolution of organic chemicals from a floating organic surface layer. To provide a conservative estimate of rates of dissolution the boundary layer model of Lewis and Whitman, was assumed to be applicable (6).

For the calculations the water boundary layer thickness was taken to be 1×10^{-4} m for a wind speed of 10 $m.s^{-1}$ and 5×10^{-6} m for a wind speed of 30 $m.s^{-1}$ (6). It should be noted that, using these values for the water boundary layer thickness, rates of dissolution were overestimated as floating organic layers have been shown to damp the turbulence in water leading to a reduction of the mass transfer coefficient of as much as 80% (7). Thus the water boundary layer thickness probably is larger and consequently the rate of dissolution is smaller than calculated on basis of the above values.

The diffusion coefficient of nonelectrolytes in water was predicted using the empirical relationship of Hayduk and Laudi (8):

$$D_1 = 3.877 \times 10^{-12} \eta_w^{-1.4} V_A^{-0.589} \qquad (1)$$

where: D_1 is the diffusion coefficient in water ($m^2.s^{-1}$),
η_w is the dynamic viscosity of water at the appropriate temperature (cP), and
V_A is the solute molar volume at normal boiling point ($m^3.mol^{-1}$).

The parameter V_A can be calculated from the molecular weight and the density or by using the method of Le Bas. Using the method of Le Bas the value of V_A can be calculated on the basis of the molecular formula and structure by adding up the values for the composing elements as indicated in Table 2.

Subsequently the mass transfer coefficient of the compound from the floating layer into water was calculated:

$$k_1 = \frac{D_1}{z_1} \qquad (2)$$

where: k_1 is the mass transfer coefficient into water ($m.s^{-1}$), and
z_1 is the water boundary layer thickness (m).

Assuming that the concentration difference of the compound over the water boundary layer is maximal, i.e. equal to the water solubility of the compound, the mass transfer flux into water is given by:

$$F_1 = k_1 \Delta c \qquad (3)$$

where: F_1 is the mass transfer flux into water ($kg.m^{-2}.s^{-1}$), and
Δc is the solubility in water ($kg.m^{-3}$).

$$At = \frac{Vs\,\rho}{F_1 + F_g} \qquad (5)$$

where: A is the real average surface area (m^2), and
t is the real exposure time, or the persistence of the floating layer (s).

In Table 3 the product of A and t is compared with that of A_a and t_v for all compounds. Unfortunately, the individual values of A and t could not be calculated as an integrated computer program was not available. Therefore, we estimated the value of these parameters assuming that they are proportionally smaller than the values of A_a and t_v. These calculated values of A and t are compared with those of A_a and t_v in Table 4.

Table 3. Comparison of the product of the average surface area and the time for disappearance of the organic surface layer through evaporation and dissolution with that for disappearance through evaporation only

Compound	Spill volume, m^3	Wind speed, $m.s^{-1}$	Surface area x time, $m^2.s$	
			evaporation and dissolution	evaporation only
Benzene	60	10	$7.6x10^6$	$7.7x10^6$
	2000	10	$2.0x10^8$	$2.0x10^8$
1,4-Xylene	60	10	$7.2x10^7$	$7.2x10^7$
	2000	10	$2.1x10^9$	$2.1x10^9$
Methyl ethylketone	60	10	$5.4x10^6$	$7.1x10^6$
	2000	10	$1.5x10^8$	$1.9x10^8$
Aniline	60	10	$1.7x10^8$	$4.0x10^8$
	2000	10	$5.4x10^9$	$1.2x10^{10}$
	2000	30	$4.6x10^8$	$5.4x10^9$
Butanol	60	10	$2.5x10^7$	$3.2x10^7$
	2000	10	$8.3x10^8$	$1.1x10^9$
Pyridine	60	10	$1.3x10^7$	$3.4x10^7$
	2000	10	$3.6x10^8$	$7.6x10^8$

The average amount of the compound that dissolves per m^2 during time t, was calculated using equation 6:

$$M_1 = F_1 t \qquad (6)$$

and the fraction of the total spill that dissolves using equation 7:

$$f = \frac{Fl}{F_1 + F_g} \qquad (7)$$

where: M_1 is the average amount of the compound that dissolves ($kg.m^{-2}$), and
f is the fraction of the total spill that dissolves.

As the real exposure time or persistence of the floating layers was calculated to be very short (less than 5 hours), it was assumed that advective and dispersive dilution does not occur during that period of time.

Table 4. Comparison of the estimated values of the average surface area and the time for disappearance of the organic surface layer through evaporation and dissolution with the values for disappearance through evaporation only

Compound	Spill volume, m^3	Wind speed, $m.s^{-1}$	Surface area, m^2		Time, hours	
			evaporation and dissolution	evaporation only	evaporation and dissolution	evaporation only
Benzene	60	10	$1.1x10^4$	$1.1x10^4$	0.20	0.20
	2000	10	$1.3x10^5$	$1.3x10^5$	0.42	0.42
1,4-Xylene	60	10	$2.2x10^4$	$2.2x10^4$	0.90	0.90
	2000	10	$3.2x10^5$	$3.2x10^5$	1.8	1.8
Methyl ethylketone	60	10	$3.6x10^3$	$1.1x10^4$	0.16	0.18
	2000	10	$1.3x10^5$	$1.5x10^5$	0.32	0.36
Aniline	60	10	$3.6x10^4$	$5.5x10^4$	1.3	2.0
	2000	10	$2.8x10^5$	$4.1x10^5$	5.4	7.9
	2000	30	$7.8x10^4$	$2.7x10^5$	1.6	5.6
Butanol	60	10	$1.6x10^4$	$1.8x10^4$	0.44	0.50
	2000	10	$2.4x10^5$	$2.7x10^5$	0.98	1.1
Pyridine	60	10	$8.2x10^3$	$1.3x10^4$	0.44	0.70
	2000	10	$1.0x10^5$	$1.5x10^5$	0.97	1.4

And then, assuming that the sea water layer with a depth of 20 or 200 m is homogeneously mixed vertically the average concentration of the compound in water immediately after that period of time, t, was calculated:

$$c = \frac{Ml}{h} \tag{8}$$

where: c is the concentration of the compound in water at time t (kg.m^{-3}), and

h is the depth of the sea water layer (m).

The volume of contaminated water after the same period of time was calculated from the real average surface area of the organic layer and the depth of the homogeneously mixed sea water layer:

$$V_1 = Ah \tag{9}$$

where: V_1 is the volume of contaminated sea water at time t (m^3).

The results of the calculations are given in Tables 5-7.

3.1.4. Natural dispersion Natural dispersion has been shown to depend on sea state, layer thickness, chemical/water interfacial tension, density difference between the chemical and seawater and viscosity of the organic material (4). The rate of this process has been found to increase with rougher seas and increasing density, and with decreasing layer thickness, decreasing interfacial tension and decreasing viscosity. On basis of the density difference it is expected that for the chemicals that are considered here dispersion may be significant only for aniline and possibly also for pyridine. Due to this process the rate of dissolution of these two compounds may be higher than the values presented in the above section.

3.2. Fate assessment of the dissolved compound

The concentration of a compound dissolved in sea water may decrease in time due to various fate processes. These processes can be transport and transformation processes. Here we will assess the effect of transport processes only. The effect of transformation processes, such as biodegradation and phototransformation, on the concentration of the dissolved compound will not be considered although this effect may be significant.

The important transport processes that may affect the concentration of a compound in sea water are dispersion and evaporation. The process of dispersion at sea has been discussed by Fischer et al. (9). They concluded that the effect of this process on the concentration of a compound in sea water is best described by the empirical relationship:

$$C_t = C_o\left[\frac{1.5}{\left(1+\frac{8\varepsilon_0 t}{b^2}\right)^3 - 1}\right]^{\frac{1}{2}} \tag{10}$$

where: C_0 is the concentration at time zero (mg.l^{-1}),

C_t is the concentration at time t (mg.l^{-1}),

t is the time (s),

b is the diameter of the contaminated water mass at time zero (m), and

ε_0 is the dispersion coefficient at time zero (m^2.s^{-1}).

The value of ε_0 can be calculated using the empirical equation:

$$\varepsilon_0 = \alpha b^{4/3} \tag{11}$$

Table 5. Assessment of the concentration in water of benzene and 1,4-xylene and of the contaminated volume of water immediately after an accidental spill at sea and after 1 and 7 days. Instantaneously spilled volumes are taken to be 60 and 2000 m^3 and calm weather conditions are assumed, i.e. wind speed is 10 $m.s^{-1}$

	Benzene		1,4-Xylene	
Spilled volume (m^3)	60	2000	60	2000
Mass transfer coefficient into water ($m.s^{-1}$)	$6.2x10^{-6}$	$6.2x10^{-6}$	$5.0x10^{-6}$	$5.0x10^{-6}$
Mass transfer flux into water ($kg.m^{-2}.s^{-1}$)	$1.1x10^{-5}$	$1.1x10^{-5}$	$9.9x10^{-7}$	$9.9x10^{-7}$
Mass transfer flux into air ($kg.m^{-2}.s^{-1}$)	$6.9x10^{-3}$	$8.7x10^{-3}$	$7.2x10^{-4}$	$8.4x10^{-4}$
Average dissolved amount of the compound ($kg.m^{-2}$)	$7.9x10^{-3}$	$1.7x10^{-2}$	$3.2x10^{-3}$	$6.4x10^{-3}$
Fraction of the total spill that is dissolved	0.0016	0.0013	0.0014	0.0012
Depth of the mixed water layer (m)	20	20	20	20
Concentration in water ($mg.l^{-1}$):				
immediately after the spill*	0.4	0.9	0.2	0.3
after 1 day*	0.09	0.4	0.05	0.2
after 7 days*	0.008	0.06	0.005	0.03
Volume of contaminated water (m^3):				
immediately after the spill**	$2.2x10^5$	$2.6x10^6$	$4.4x10^5$	$6.4x10^6$
after 1 day**	$9.0x10^5$	$5.2x10^6$	$1.5x10^6$	$9.8x10^6$
after 7 days**	$1.0x10^7$	$4.1x10^7$	$1.5x10^7$	$6.8x10^7$
$t_{½}$ for evaporation of dissolved compound (days)**	11	11	14	14

* For a depth of 200 m the concentrations have to be divided by a factor of 10.

** For a depth of 200 m the volumes and the half-life have to be multiplied by a factor of 10.

Table 6. Assessment of the concentration in water of methyl ethylketone and butanol and of the contaminated volume of water immediately after an accidental spill at sea and after 1 and 7 days. Instantaneously spilled volumes are taken to be 60 and 2000 m^3 and calm weather conditions are assumed, i.e. wind speed is 10 $m.s^{-1}$

	Methyl ethylketone		Butanol	
Spilled volume (m^3)	60	2000	60	2000
Mass transfer coefficient into water ($m.s^{-1}$)	$6.2x10^{-6}$	$6.2x10^{-6}$	$5.9x10^{-6}$	$5.9x10^{-6}$
Mass transfer flux into water ($kg.m^{-2}.s^{-1}$)	$2.2x10^{-3}$	$2.2x10^{-3}$	$4.5x10^{-4}$	$4.5x10^{-4}$
Mass transfer flux into air ($kg.m^{-2}.s^{-1}$)	$6.8x10^{-3}$	$8.4x10^{-3}$	$1.5x10^{-3}$	$1.5x10^{-3}$
Average dissolved mass of the compound ($kg.m^{-2}$)	1.3	2.5	0.71	1.6
Fraction of the total spill that is dissolved	0.24	0.21	0.23	0.23
Depth of the mixed water layer (m)	20	20	20	20
Concentration in water ($mg.l^{-1}$):				
immediately after the spill*	65	125	36	80
after 1 day*	16	67	10	50
after 7 days*	1.4	8.5	0.9	7.0
Volume of contaminated water (m^3):				
immediately after spill**	$1.9x10^5$	$2.6x10^6$	$3.2x10^5$	$4.8x10^6$
after 1 day**	$9.2x10^5$	$5.6x10^6$	$1.3x10^6$	$8.6x10^6$
after 7 days**	$1.1x10^7$	$4.4x10^7$	$1.4x10^7$	$6.2x10^7$
$t_{½}$ for evaporation of dissolved compound (days)**	69	69	250	250

* For a depth of 200 m the concentrations have to be divided by a factor of 10.

** For a depth of 200 m the volumes and the half-life have to be multiplied by a factor of 10.

Table 7. Assessment of the concentration in water of pyridine and aniline and of the contaminated volume of water immediately after an accidental spill at sea after 1 and 7 days. Instantaneously spilled volumes are taken to be 60 and 2000 m^3 and calm weather conditions are assumed, i.e. wind speed is 10 $m.s^{-1}$

	Aniline		Pyridine		Aniline***
Spilled volume (m^3)	60	2000	60	2000	2000
Mass transfer coefficient into water ($m.s^{-1}$)	$6.0x10^{-6}$	$6.0x10^{-6}$	$6.3x10^{-6}$	$6.3x10^{-6}$	$1.2x10^{-4}$
Mass transfer flux into water ($kg.m^{-2}.s^{-1}$)	$2.0x10^{-4}$	$2.0x10^{-4}$	$2.8x10^{-3}$	$2.8x10^{-3}$	$4.1x10^{-3}$
Mass transfer flux into air ($kg.m^{-2}.s^{-1}$)	$1.6x10^{-4}$	$1.8x10^{-4}$	$1.8x10^{-3}$	$2.6x10^{-3}$	$3.8x10^{-4}$
Average dissolved amount of the compound ($kg.m^{-2}$)	0.94	3.9	4.4	9.8	23.6
Fraction of the total spill that is dissolved	0.56	0.53	0.61	0.52	0.92
Depth of the mixed water layer (m)	20	20	20	20	20
Concentration in water ($mg.l^{-1}$):					
immediately after the spill*	47	195	220	490	1180
after 1 day*	19	136	56	263	738
after 7 days*	2.1	20	5.0	33	103
Volume of contaminated water (m^3):					
immediately after the spill**	$7.2x10^5$	$5.6x10^6$	$1.6x10^5$	$2.0x10^6$	$5.4x10^6$
after 1 day**	$2.7x10^6$	$1.2x10^7$	$1.0x10^6$	$5.6x10^6$	$8.6x10^6$
after 7 days**	$2.5x10^7$	$7.9x10^7$	$1.2x10^7$	$4,4x10^7$	$6.2x10^7$
t½ for evaporation of dissolved compound (days)**	1200	1200	375	375	450

* For a depth of 200 m the concentrations have to be divided by a factor of 10.

** For a depth of 200 m the volumes and the half-life have to be multiplied by a factor of 10.

*** Stormy weather conditions (wind speed 30 $m.x^{-1}$) and a spill volume of 2000 m^3

where: α is a dispersion factor ($m^{2/3}.s^{-1}$).

The value of α has been found to range from 1.5×10^{-5} to 2.7×10^{-4} $m^{2/3}.s^{-1}$ the average value being 7×10^{-5} $m^{2/3}.s^{-1}$ (10,11). Based on this average value the concentration of the compounds in sea water after 1 and 7 days was calculated. The results are presented in Tables 5-7.

The rate of evaporation of the dissolved compound from water was calculated using the program VRDAMP (6). The physico-chemical data needed for this calculation are the diffusion coefficient in water and in air and Henry's law constant. The value of the diffusion coefficient of the compounds in water was calculated using equation 1. The value of the diffusion coefficient in air was assumed to be 10^4 times the diffusion coefficient in water. Henry's law constant was calculated from the solubility in water and the vapour pressure which data are given in Table 1. The environmental parameters needed as input for the program VRDAMP are the wind speed (10 or 30 $m.s^{-1}$), the water depth (20 or 200 m) and the water temperature (10°C). The results of the calculations, expressed as $t_{\frac{1}{2}}$, are given also in Tables 5-7.

4. EXPOSURE RATING

Despite the uncertainties involved the results as presented in Tables 2-4 may well be used for ranking of compounds for hazard assessments. The results unambiguously demonstrate that the exposure of aquatic organisms is different for different compounds depending on their physico-chemical properties. In this respect the important physico-chemical properties of a compound are the density, influencing the process of spreading, the boiling point (what parameter is closely related to the vapour pressure), influencing the process of evaporation from the surface layer, and the solubility, influencing the process of dissolution.

When more (and more accurate) data are available such a ranking may well be based on simple relationships between these physico-chemical properties and the exposure of aquatic organisms to the compound instead of the complex calculation procedure used here. Such a relationship may involve the concentration of the compound in water immediately after the spill related to the boiling point, the density and the solubility such as the relationships that we established for the results presented in Tables 5-7 (see also Figure 1):

-for a spill of 60 m^3:

$$c = 8.44 \times 10^{-18} (Bp \times \rho \times S^{0.35})^{2.58} \qquad (12)$$

-and for a spill of 2000 m^3:

$$c = 2.47 \times 10^{-18} (bp \times \rho \times S^{0.35})^{2.73} \qquad (13)$$

where: c is the concentration in water ($kg.m^{-3}$),
Bp is the boiling point of the compound (°C),
ρ is the density of the compound ($kg.m^{-3}$), and
S is the solubility of the compound in water ($mol.m^{-3}$).

For ranking purposes also a relationship between the fraction of the spilled compound that dissolves and these physico-chemical properties may be useful. On basis of the results presented in Tables 5-7 we derived a linear relationship (see also figure 2):

$$f = -0.1625 + 1.13 \times 10^{-6} (Bp \times \quad \times S^{0.20}) \qquad (14)$$

This relationship indicates that:
- less than 1% of the total mass of the compound dissolves when: $Bp \times \rho \times S^{0.20} < 1.53 \times 10^5$
- between 1 and 10% of the total mass of the compound dissolves when: $1.52 \times 10^5 < Bp \times \rho \times S^{0.20} < 2.32 \times 10^5$
- more than 10% of the total mass of the compound dissolves when: $Bp \times \rho \times S^{0.20} > 2.32 \times 10^5$

This relationship, however, can be improved since in its present form it is not exclusively restricted to the fraction range of 0 to 1.

It is clear that chemicals that dissolve in water after a spill for less than 1% pose a lower hazard to water organisms than those dissolving between 1 and 10% because their exposure to the spilled chemical is more limited. The same but even stronger applies to the chemicals that dissolve between 10 and 100% in water.

5. HAZARD RATING

The GESAMP-WG has ranked chemicals according to their aquatic toxicity as shown in Table 8.

Table 8. GESAMP-aquatic toxicity rating of bulk chemicals transported by sea (1)

rating	description	acute LC50 (mg/l)
4	highly toxic	1
3	moderately toxic	1-10
2	slightly toxic	10-100
1	practically non toxic	100-1000
0	insignificant toxic	1000

The aquatic toxicity of chemicals can be determined experimentally and the acute LC50 (after e.g. 24, 48 or 96 hrs) estimated. The applied rating although arbitrarely, is practical and covers a wide range using steps of one order of magnitude.

Using also steps of one order of magnitude with respect to the percentage of organic chemical that dissolves in sea water after a spill of a chemical tanker, both the toxicity rating and exposure rating can be combined into a hazard rating as described in Table 9.

Because of the simplicity of the proposal for incorporatio of exposure, it will take relatively little work to transform the available GESAMP toxicity ratings for chemicals transported in bulk by ship into environmentally more realistic hazard ratings. It is recommended to use the hazard rating as described above for the allocation of the ship type in which a chemical should be transported in bulk by ship at sea.

Table 9. Integration of the exposure classification and the GESAMP toxicity rating into a hazard rating

product	GESAMP toxicity rating	Exposure rating	Resultant hazard rating
Benzene	2	-2	0
Xylene	2	-2	0
White Spirit	3	-1	2
MEK	0	0	0
Butanol	1	0	1
Aniline	2	0	2
Pyridine	1	0	1

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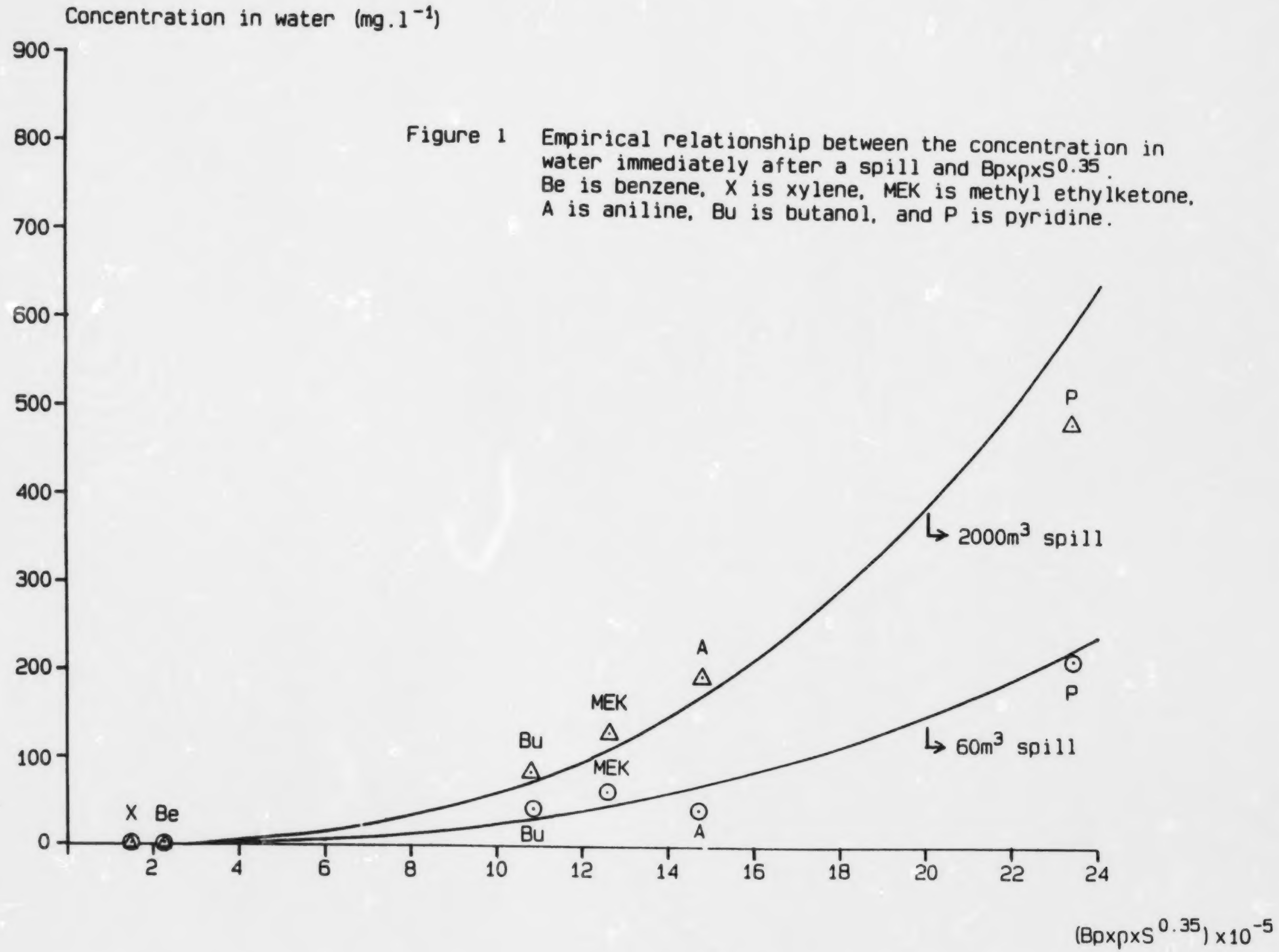
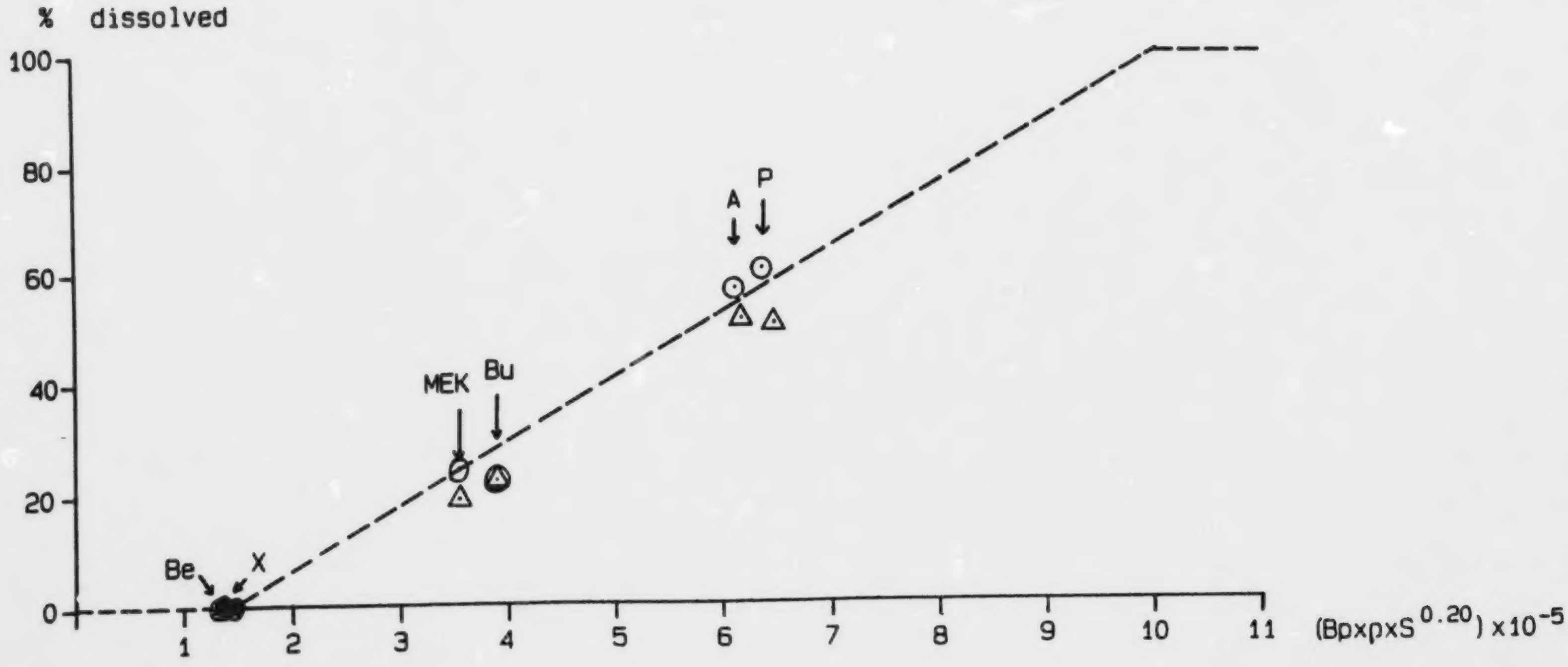


Figure 1 Empirical relationship between the concentration in water immediately after a spill and BpxρxS$^{0.35}$. Be is benzene, X is xylene, MEK is methyl ethylketone, A is aniline, Bu is butanol, and P is pyridine.

Figure 2 Empirical relationship between the percentage of the total mass of the compound that dissolves and $B\rho x \rho x S^{0.20}$ for spills of 60m^3 (⊙) and 2000m^3 (△)



HEAVY GAS DISPERSION MODELLING FOR HAZARD AND RISK ASSESSMENT

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INTRODUCTION

In recent years a number of accidental releases of toxic or flammable gases into the atmosphere has drawn attention to the need for better emergency planning to avert undesirable outcomes. The Mississauga train derailment resulting in the release of toxic chlorine gas into the atmosphere in November, 1979, emphasized the great dangers and necessary tactical responses often associated with such catastrophic events. The tragic accident in Bhopal, India in 1984, where close to 3,000 people perished of methyl isocynate poisoning, is a further attestation to the possible severity of such outcomes.

The increased use of liquefied gases as a source of energy or chemical feedstock, justifies the need to develop and maintain practical and well-tested heavy-gas dispersion models for estimating zones of risk resulting from accidental chemical spillage. These models can in turn be employed in the assessment of the potential hazards associated with such accidents, and, more importantly, to assist in the development of an appropriate emergency response plan for present and newly proposed manufacturing, transportation, and storage facilities.

In response to these specific needs, Concord Scientific Corporation, with financial support from Environment Canada, Atmospheric Environment Service (AES), has developed a state-of-the-art heavy-gas spill and dispersion model (COBRA), which was designed primarily to simulate Liquefied Natural Gas (LNG) spills (Alp et al., 1985). Since then numerous extensions to the model have been made. It is the purpose of this paper to present these extensions, along with a more comprehensive validation of the present model version (COBRA II) using Shell's Maplin Sands field data for both LNG and Liquefied Petroleum Gas (LPG) (Puttock and Colenbrander, 1985). The paper also discusses the use of COBRA II in a recently developed Comprehensive Hazard Assessment System for Estimating Risk (CHASER) due to spills of heavy-gas-producing chemicals during their manufacture, transportation or storage. This integrated risk assessment system has been successfully used in part in two case studies, one involving the transportation of LPG by ship and the other involving the construction of a natural gas liquid (NGL) plant, both near populated areas.

DESCRIPTION OF ORIGINAL MODEL COBRA

Briefly, COBRA treats the gas source, whose size (radius) and gas emission rate have been determined by the pool spread and gas generation module, as a steady idealized rectangular source of equivalent area. Over the source, gravity spread is neglected and a Gaussian concentration profile is assumed in the vertical. If the emitted gas cannot be taken up completely by the wind, which is assumed to have a power law profile, then a pure gas blanket is allowed to form over the liquid pool. This gas blanket also spreads by gravity. Its size, determined in a similar manner to the liquid pool, is, in turn, taken as the size of the gas source. At the downwind edge of the source, the horizontal concentration profile is assumed uniform. This uniform core spreads in the lateral direction under the influence of gravity and turbulent diffusion. The plume concentration distribution at the lateral edges is assumed to be Gaussian. Further downwind, the uniform central core is completely spent and a smooth transition to passive Gaussian dispersion is provided. The treatment of heat transfer and humidity is facilitated through the use of mass and energy balances performed on a vertical slice of the plume perpendicular to the flow direction.

The model also treats transient gas releases, i.e., releases in which the area of the gas source varies with time. This is accomplished by using "observers" which take up gas as they pass over the gas source. A steady state calculation is then made for each observer. By knowing the location of each observer as a function of time, it is possible to determine flammable cloud hazard zones due to contributions from successive "observers" at any desired time.

COBRA requires meteorological information during the release, such as wind speed, stability, air and surface temperature, as well as information on the type (e.g., instantaneous, finite time, continuous) and size of spill, the type of surface (e.g., land, water, open, confined) on which the spill occurs, the surface roughness of the terrain over which dispersion is assumed to take place, and of course the spilled material.

Outputs from COBRA include the maximum hazard zone length, width, and height, and their corresponding times from spill initiation, as well as plots of hazard zones for these times. Hazard zones are based on input hazard limits in terms of volume fractions for the materials of interest.

COBRA is suitable for continuous or finite time releases of heavy-gas-producing liquids and/or heavy vapours, as well as instantaneous releases of heavy-gas-producing liquids, although the original version has only been adapted for the latter type of releases. It is not suitable for instantaneous releases of gaseous materials. It is applicable to dispersion over homogeneous flat terrain and does not handle flow disturbances due to obstructions such as buildings or ridges.

MODEL EXTENSIONS: DESCRIPTION OF COBRA II

In the pursue of generalizing COBRA's capabilities as a heavier-than-air-gas dispersion model, numerous extension modules have been included in COBRA; resulting with the present form, COBRA II. Since the last reporting of COBRA (Alp et al., 1985), the model has been modified to handle (1) constant and highly time variable spill rates of finite duration, (2) land spills, (3) confined spills, (4) simultaneous liquid and gas releases and (5) chemical spills other than the LNG spills reported earlier.

Constant and Time Varying Spill Rates

In COBRA, the amount of liquid remaining on the surface $V[m^3]$ is defined in terms of a differential mass balance equation:

$$\frac{dV}{dt} = \dot{V}_c - \frac{\dot{m}}{\rho}, \qquad (V(0) = V_i) \qquad (1)$$

with V_i = initial volume spilled $[m^3]$,
$\dot{V}_c$ = volumetric spill rate, which may be a function of time $[m^3/s]$,
$\dot{m}$ = evaporation rate $[kg/s]$,

ρ = liquid density (assumed constant and uniform) [kg/m^3],
t = time elapsed since the initiation of spill [s].

By prescribing a value to $\dot{V}_c$ in Equation (1) other than zero, as is taken to be the case in an instantaneous release, a continuous inflow of liquid to the pool is assumed. The growth of the liquid pool and thus the evaporation rate (e.g., $\dot{m} = A\,\dot{m}''$ for unconfined spills on water, where A is the pool area and $\dot{m}''$ is a time independent empirical evaporation flux [kg/(m^2•s)]) from the pool is intrinsically limited by the flow rate of the liquid to the pool.

It has been shown that, the time dependent spill rate of a liquid from a container that has been involved in an accident can be approximated by the following generalized fourth-order polynomial (Oliverio, 1985)

$$\dot{V}_c = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^3 \qquad (2)$$

where a_i = empirically obtained coefficients based on the accident and container type,

and

t = time elapsed since spill initiation.

The coefficients of the fourth-order equation are a function of the type and size of the storage vessel, final hole size and configuration, tear configuration (smooth or jagged), cargo, ambient temperature (which essentially defines internal pressure), and containment method (pressurized or refrigerated). For the trivial case, $\dot{V}_c$ can be assumed constant with time. Since at time t = 0 no material has yet been deposited on the surface, $V(0)=V_i= 0$. The flow rate can be ceased whenever desired by specifying a termination time. Equation (2) is used in COBRA II with manual input of the coefficients depending on the scenario under investigaion.

Land Spill

For liquefied gas spills on land, an important heat source to the liquid pool is the ground. The rate of heat transfer from the ground to the liquid pool is regulated primarily by the rate of heat conduction through the ground.

For a spreading liquid pool, the successive annular "growth" elements of the pool remain in contact with the ground for varying time periods, necessitating, for the sake of realism, that the evaporation rate equation used in COBRA permit for these differences in exposure times. For spills on land, the evaporation rate $\dot{m}$ is based on Briscoe and Shaw's (1980) model,

$$\dot{m} = c_2 \frac{K_g\,(T_{go} - T_b)}{\lambda\,(\pi\alpha_g)^{1/2}} \int_0^{R_s(t)} \frac{2\pi r'}{(t-t')^{1/2}}\,dr', \qquad (3)$$

where c_2 = 3, an empirical parameter to account for uncertainties in ground thermodynamic properties and texture,
K_g = thermal conductivity of soil [W/(M•K)],
T_{go} = initial temperature of the ground [°C],
T_b = boiling point of liquefied chemical [°C],
λ = latent heat of vaporization of liquefied chemical [J/kg],
α_g = thermal diffusivity of soil [m^2/s],
r' = $\int_0^{t'} (\frac{dr}{dt})dt$, where t' is the arrival time of the spreading pool at radius r'.

Because the ground does not act as an infinite source of heat to the liquid pool the evaporation flux $\dot{m}''$ from the pool inherently declines with time (Figure 1).

Confined Spills

Clearly, to simulate a confined spill the maximum "confinement" radius [m] desired by the user must be pre-defined and entered as an input parameter to the model.

Simultaneous Liquid and Gas Releases

In real life situations, the liquid and gaseous release of the chemical often occur simultaneously. With the inclusion of two-phase releases in COBRA, the prediction of the hazard zones are generally felt to be more realistic.

COBRA II: More Than a LNG Model

COBRA II is presently suitable to simulate methane, butane, propane and chlorine releases.

COBRA II - DATA/MODEL COMPARISON

COBRA II has been tested by comparing the model predictions against published 1980 Maplin Sands field data, as well as against reported predictions of Colenbrander's HEGADAS II (Puttock and Colenbrander, 1985), DEGADIS (Havens and Spicer, 1985) and FEM3 (Chan and Ermak, 1985). The validation runs are summarized in Table 1. For comparison purposes, a 5.0 % lower flammability limit (LFL) for the methane runs and a 2.1 % limit for those of propane were employed for estimating the zones of risk associated with the spills. Normally, 50 % of the LFL is used in delineating the hazard zones in order to amend for discontinuities in the plume.

Two relatively simple error statistics have been calculated for each of the models (Table 1): (1) the mean relative error

$$MRE = \frac{1}{n} \sum_{i=1}^{n} \frac{P_i - O_i}{O_i} , \qquad (4)$$

where P_i = model predictions,
O_i = field observations,
and
n = sample size,
and, (2) the mean absolute relative error

$$MARE = \frac{1}{n} \sum_{i=1}^{n} \frac{|P_i - O_i|}{O_i} . \qquad (5)$$

Further statistics are not warranted because of the small data set used for comparison. In Figures 2a and 2b the hazard-length predictions for each model are plotted against the field observations.

For COBRA II and HEGADAS II, one of the basic model assumptions, namely that advection in the mean wind direction is much larger than diffusion and gravitational spreading, breaks down for low wind speeds. As expected, the

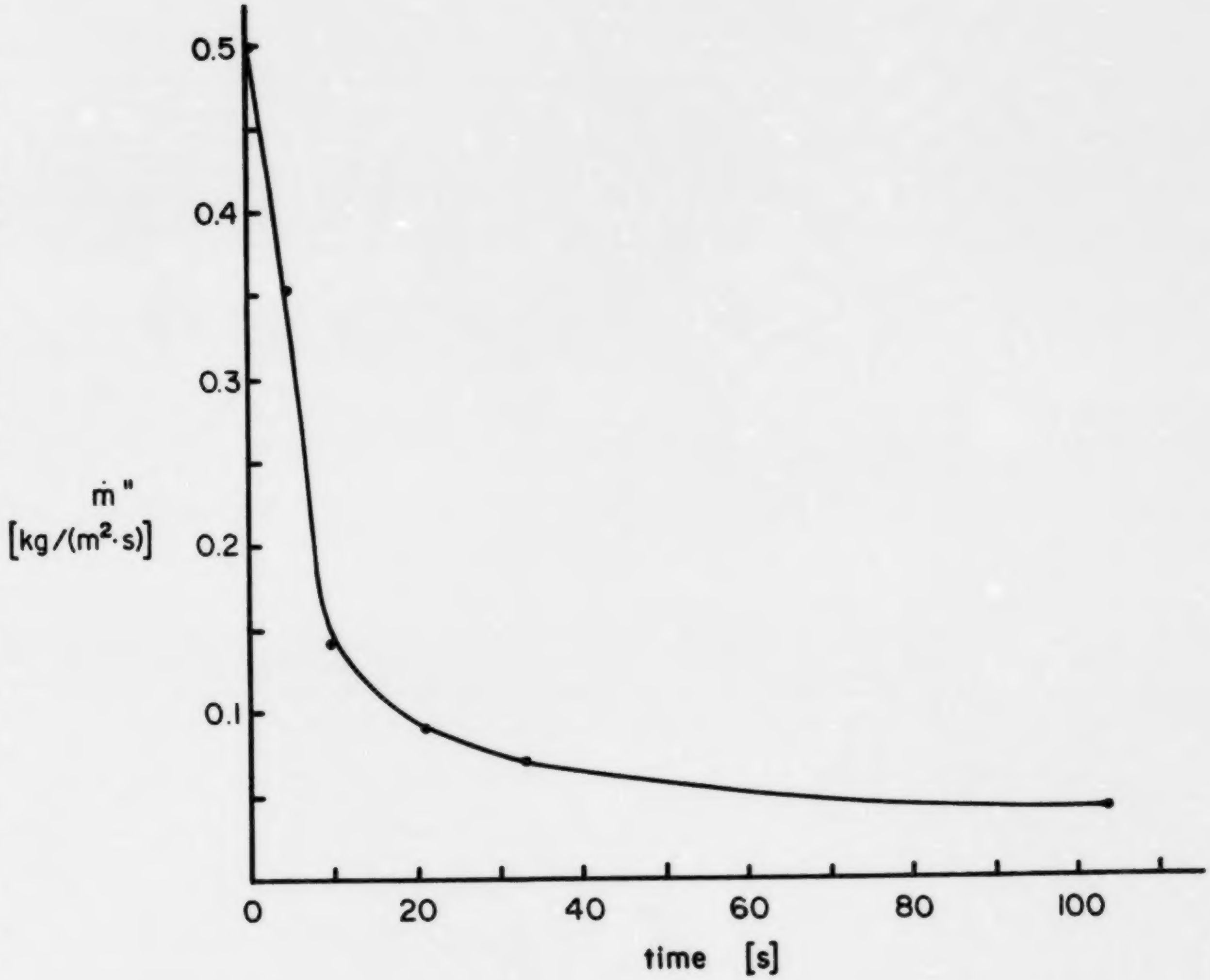

FIGURE 1. TRANSIENT VARIATION OF THE EVAPORATION FLUX $\dot{m}''$ FOR A TYPICAL UNCONFINED LAND SPILL (PROPANE) SCENARIO.

TABLE 1a

SUMMARY OF RESULTS
(Methane Runs)

		HAZARD ZONE LENGTH . . . (m)				
Run No.	U_o (m/s)	Maplin Sands (obs. to LFL)[1]	COBRA II Prediction (5 %)	HEGADAS II Prediction[1] (5 %)	DEGADIS Prediction[2] (5 %)	FEM3 Prediction[3] (5 %)
09	8.9	150 ± 25	133	101	-	-
12	1.5	67 ± 5	44	55	-	-
15	3.6	175 ± 30	79	121	-	-
27	5.5	200 ± 25	217	242	210	-
34	8.6	170 ± 25	173	193	140	-
35	9.8	180 ± 30	239	204	140	-
39	4.1	130 ± 20	203	283	300	
56	5.1	115 ± 30	96	143	160	-
29	7.4	165 ± 20	239	250	190	-
MRE %			3.0	17.8	25.0	-
MARE %			29.0	35.9	38.3	-

[1] Puttock and Colenbrander, 1985
[2] Havens and Spicer, 1985
[3] Chan and Ermak, 1985

TABLE 1b

SUMMARY OF RESULTS
(Propane Runs)

		HAZARD ZONE LENGTH . . . (m)				
Run No.	U_o (m/s)	Maplin Sands (obs. to LFL)[1]	COBRA II Prediction (2.1%)	HEGADAS II Prediction[1] (2.1%)	DEGADIS* Prediction[2] (2.1%)	FEM3 Prediction[3] (2.1%)
43	5.5	215 ± 20	221	244	218	-
46	8.1	230 ± 35	192	225	195	-
47	5.6	235 ± 25	339	322	290	220
49	6.2	270 ± 25	203	211	190	140
50	7.9	$220 \begin{smallmatrix} +40 \\ -30 \end{smallmatrix}$	264	278	240	190
54	3.8	450 ± 70	257	294	260	270
MRE %			-2.9	3.0	-8.9	-27.0
MARE %			25.2	22.6	20.1	27.0

* Extracted from available graphical information (Havens and Spicer, 1985)

[1] Puttock and Colenbrander, 1985
[2] Havens and Spicer, 1985
[3] Chan and Ermak, 1985

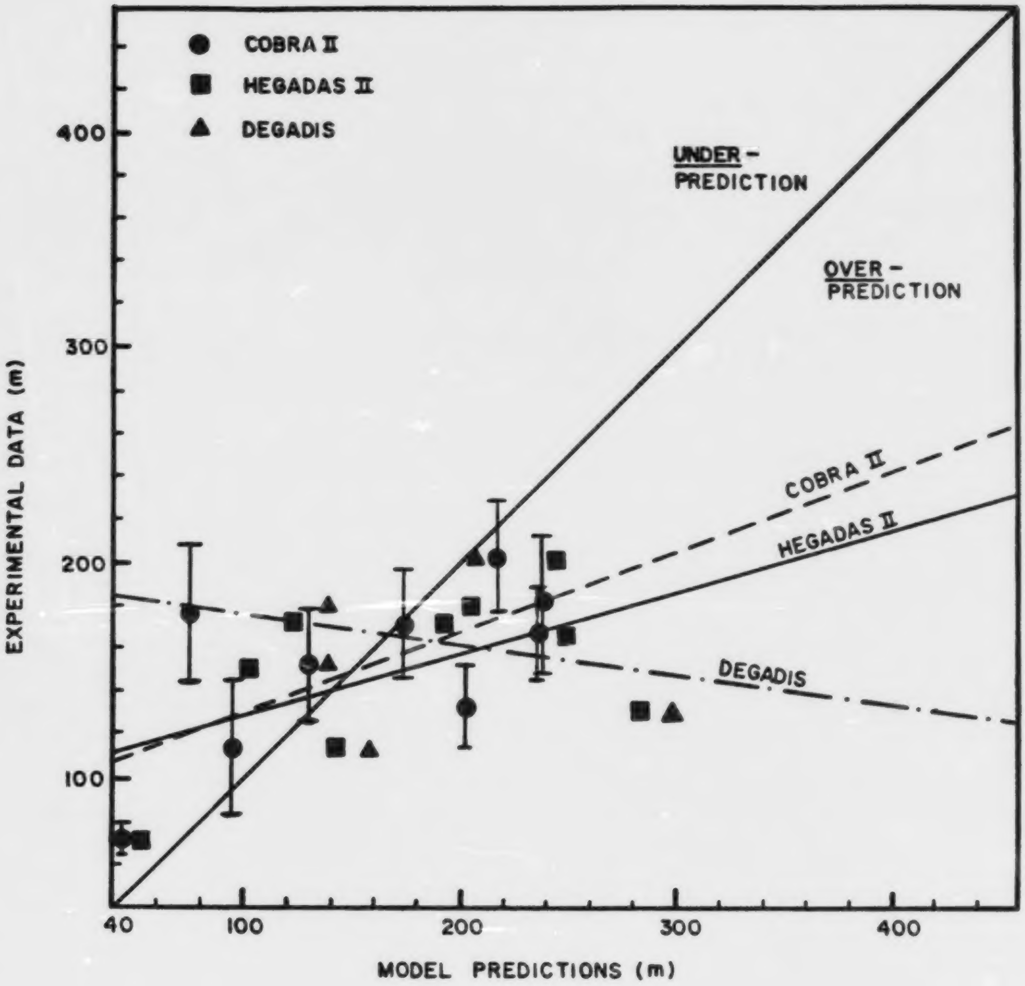

FIGURE 2a. PREDICTIONS VERSUS EXPERIMENTAL DATA OF DOWNWIND HAZARD LENGTHS FOR 9 METHANE RUNS.

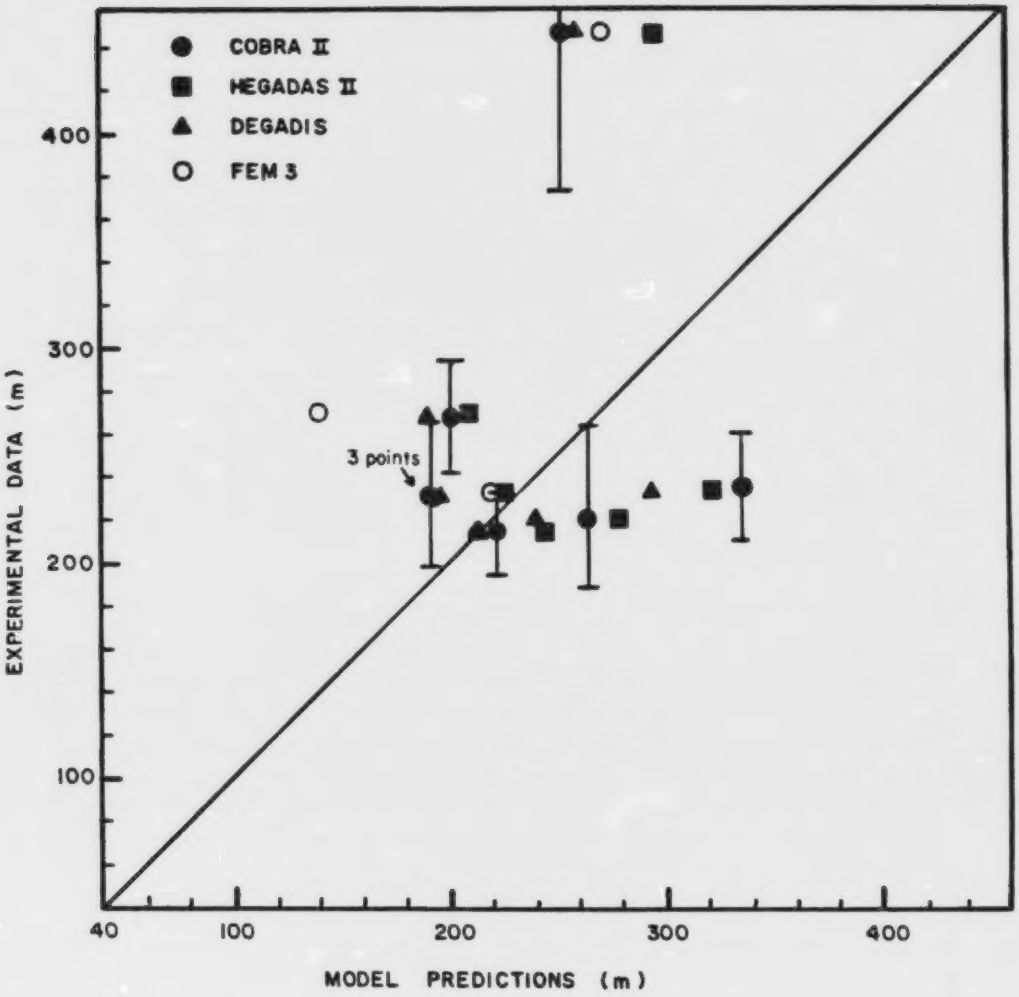

FIGURE 2b. PREDICTIONS VERSUS EXPERIMENTAL DATA OF DOWNWIND HAZARD LENGTHS FOR 6 PROPANE RUNS.

two models underpredict the hazard zone at this end (Runs 12 and 15). The other underpredictions for COBRA II seem to be within the experimental error bounds. Clearly, better capability is required in COBRA II for near-calm conditions.

In Figure 2a, prediction trends are established for each of the models by simple linear regression. It is worth noting that, less emphasis should be placed on the trend line obtained for the DEGADIS model because of the clustering of the data points at the larger hazard zones (i.e., no information is available at the lower end).

No discernible trends can be obtained from Figure 2b because of the clustering of the data and the presence of the possible "outliers" at the top of the graph. Additional information is certainly necessary to warrant further investigation.

The prediction trends established in Figure 2a generally agree well with the calculated MRE values (Table 1a.) All models overpredict on the average. COBRA II, however provides better maximum hazard length estimates on average for methane releases than do the other two models. For the propane runs, COBRA II slightly underpredicts (MRE = -2.9 %), but is generally at par with HEGADAS II, which exhibits a slight overprediction (MRE = 3.0 %).

Offered in Figure 3 is the visible limits of COBRA II-predicted and observed plume configuration for spill 29.

APPLICABILITY OF COBRA II FOR RISK ASSESSMENT

Application of COBRA II in CHASER

A Comprehensive Hazard Assessment System for Estimating Risk (CHASER) has been under development by Concord Scientific Corporation for dealing with potential releases of hazardous chemicals during transportation, storage, or manufacture of such chemicals. It is designed for use in emergency planning. The system is comprised of four basic modules: Source module, pool spread and evaporation module, hazard assessment module, and probabilistic risk assessment module (Figure 4). Each module, in turn, consists of different state-of-the-art models for different spill situations such as pressurized or cold releases of liquefied chemicals, instantaneous, continuous, or finite time releases, releases from tanker railcars, trucks, large marine tankers, storage vessels or process units, releases of liquids on land or water, etc. Most of the individual models in each module have been computerized. They use data from a physical properties data base. The system has been designed to be general, however the thrust in its development so far has been for liquefied gases such as methane, propane, butane, chlorine, and ammonia.

The source module includes models for discharges of liquids and/or gases from storage vessels.

The pool spread and gas generation module is specifically designed for estimating the size of the liquid pool due to a liquid spill as a function of time. The spread is based on a balance of gravity and inertial forces, simultaneously taking into account boil-off of the liquid due to heat transfer from the surface on which the spill occurs.

The hazard assessment module consists of sub-modules for atmospheric dispersion, pool fires, fireballs, unconfined vapour cloud explosions (UVCE) and jet fires, and is used primarily to estimate the zones of various hazards such as toxicity, thermal radiation, explosion, or flammable clouds, due to various chemical releases. COBRA II is the cornerstone of the atmospheric dispersion sub-module.

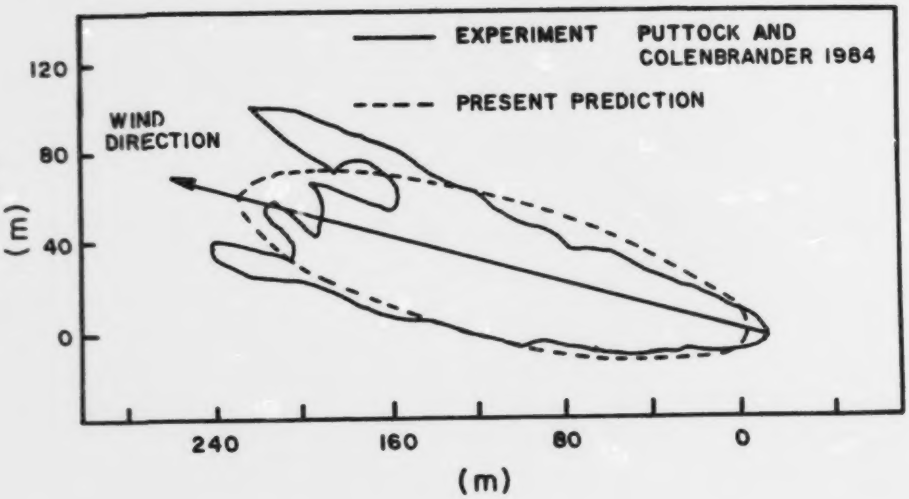

FIGURE 3. A PLAN VIEW OF THE SPILL 29 PLUME WITH THE LIMITS OF THE VISIBLE PLUME PREDICTED BY COBRA II.

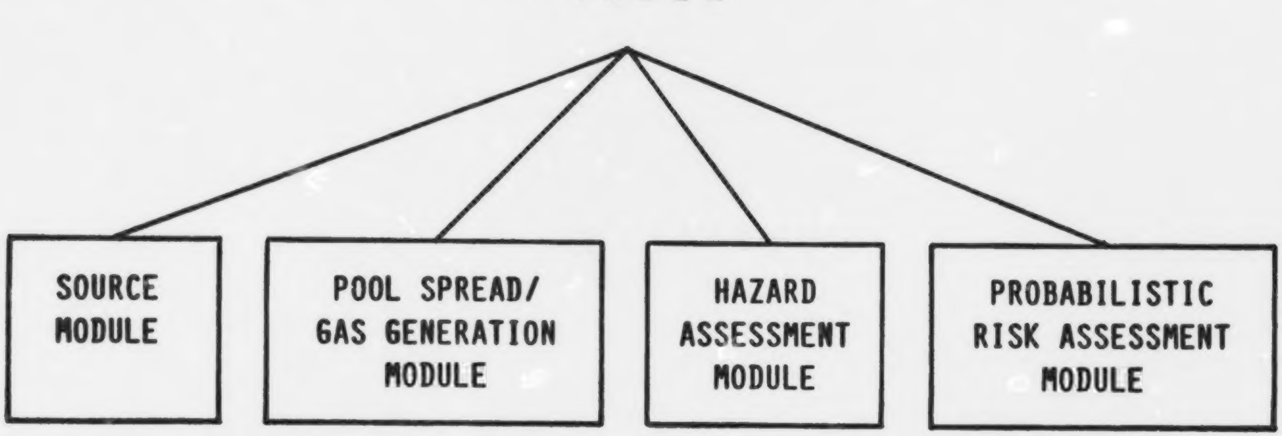
CHASER
SOURCE MODULE
POOL SPREAD/ GAS GENERATION MODULE
HAZARD ASSESSMENT MODULE
PROBABILISTIC RISK ASSESSMENT MODULE

FIGURE 4. SCHEMATIC DESCRIPTION OF CHASER.

The fourth module, or the probabilistic risk assessment module, consists of a system of manual procedures for estimating the probabilities of occurrence of release situations during the manufacture, transport, and distribution of chemicals of interest. The procedures use fault and event trees as well as historical accident and component reliability data to estimate the probabilities of occurrence. These probabilities are then combined with the hazard zones obtained from the hazard assessment module, and weather frequency, population distribution and land use data, to estimate the final risk due to potential releases of chemicals.

Sample Runs of COBRA II

Figure 5 illustrates the change of the hazard area with time for a typical release. The large circle shown has its radius equal to the maximum extent that a gas cloud of critical concentrations would travel under any weather condition and is usually termed the hazard zone. For any specific release the gas cloud would cover only a very small portion of the hazard zone at any given time.

The hazard zones associated with a 40 m^3 release of methane, butane, propane and chlorine are illustrated in Figure 6. The hazard zones shown correspond to the large circle shown in the previous figure. Chlorine's toxic nature even at low concentrations, is readily reflected in the relatively large hazard zone estimated by the model. Methane's "lightness," on the other hand, promotes a small hazard zone because of the increased vertical dispersion of the gas. Propane and butane exhibit similar physical properties (i.e., both remain heavier than air), but because propane maintains a significantly larger boil-off rate than does butane due to its lower boiling point, more propane material is released to the atmosphere at any one time. Both gases, because they remain denser than air, undergo less vertical diffusion than methane, but propane leads to a larger hazard zone essentially due to the larger gas generation rate from the liquid pool.

CONCLUSION AND RECOMMENDATIONS

A review of COBRA II was made. The COBRA II predictions were compared to a series of experimental data and three other heavy-gas dispersion models. The overall performance of COBRA II was generally as good as or better than the other models. For low wind speeds predictions are available only for two of the models. Both models underpredict under these conditions because of a breakdown of basic model assumptions.

For improvement and generalization of COBRA II, two recommendations are offered here:

1. It is recommended that a model that includes the effects of gravitational spread and diffusion in the mean wind direction at near-calm conditions be incorporated in COBRA II.
2. It is also recommended that the present version of the model be further tested against a more complete data set.

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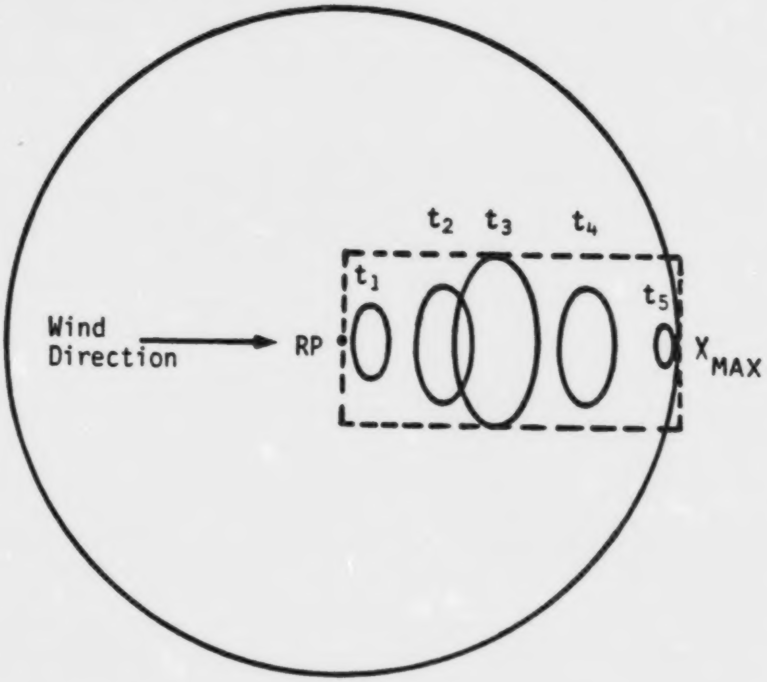
TOXICITY/FLAMMABILITY HAZARD ZONES



- RP = RELEASE POINT
- X_{MAX} = MAXIMUM DOWNWIND DISTANCE TO TOXIC/FLAMMABLE LIMIT (E.G. IDLH/.5 LFL)
- CIRCLE DEFINES TOXICITY/FLAMMABILITY HAZARD ZONE
- RECTANGLE DEFINES HAZARD ZONE FOR EVACUATION PURPOSES IF WIND DIRECTION IS KNOWN AND IS STEADY

FIGURE 5. HAZARD ZONES DUE TO A TYPICAL RELEASE.

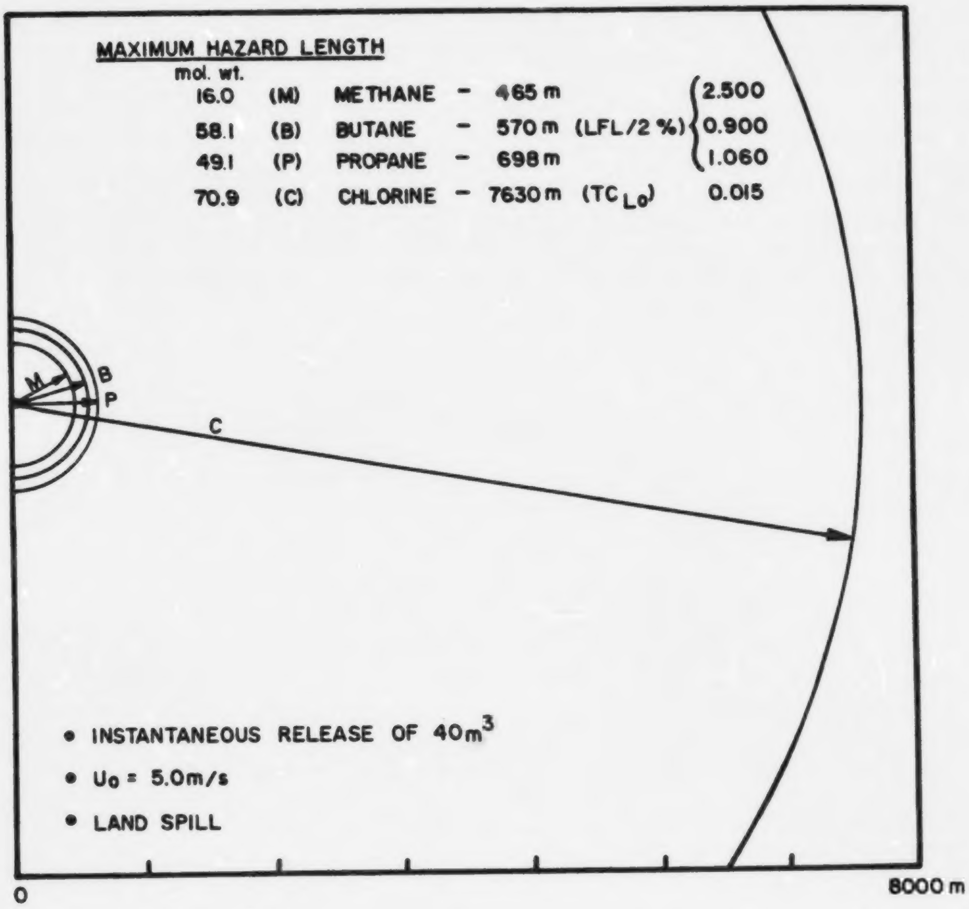

MAXIMUM HAZARD LENGTH
mol. wt.
16.0 (M) METHANE - 465 m
58.1 (B) BUTANE - 570 m (LFL/2 %)
49.1 (P) PROPANE - 698 m
70.9 (C) CHLORINE - 7630 m (TC$_{Lo}$)
2.500
0.900
1.060
0.015
M
B
P
C
• INSTANTANEOUS RELEASE OF 40m^3
• U$_0$ = 5.0m/s
• LAND SPILL
0
8000 m

FIGURE 6. SCHEMATIC REPRESENTATION OF THE MAXIMUM HAZARD LENGTH ASSOCIATED WITH A 40 m^3 RELEASE OF METHANE, BUTANE, PROPANE AND CHLORINE, AS CALCULATED BY COBRA II (LFL = LOWER FLAMMABILITY LIMIT; TC_{Lo} = LOWEST PUBLISHED TOXIC CONCENTRATION).

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A COMPUTER MODEL FOR PREDICTING OUTFLOW RATES FROM DAMAGED CHEMICAL STORAGE AND TRANSPORTATION TANKS

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ABSTRACT

A computer model has been developed to predict the outflow rate and duration of leaks from damaged chemical storage and transportation tanks. The model is simple to use and requires no knowledge of chemical properties beyond name and the mass in the tank. The model predicts chemical properties, outflow rates, tank temperatures and spill duration for ammonia, benzene, chlorine and hydrogen sulphide. Example leak nomographs are provided for these chemicals for ruptures above and below the liquid level in a standard rail tank car. Major differences between the EnviroTIPS nomographs and the computer model are noted for the case of liquified gas tanks with ruptures in the vapour space.

Recommendations arising from the project include a small or meso-scale test program to validate the model and the inclusion of more chemicals.

The study was funded by the Environmental Protection Service of Environment Canada. Mr. M.F. Fingas of the Environmental Emergencies Technology Division was the Scientific Authority.

INTRODUCTION

A simple, yet accurate technique is needed to predict the rate at which chemicals (liquid or gaseous) leak from damaged storage or transportation containers. Accurate predictions of the outflow rate and duration of the incident are vital for the planning of a safe and effective emergency response. Of particular importance to the response effort is the "source strength" component of the release. This source term is required by all atmospheric dispersion models which predict the areas which should be evacuated due to the release of the hazardous chemical.

Nomograms for predicting these chemical leak rates and durations were developed for the EnviroTIPS series of manuals (Environment Canada, 1983). Unfortunately many simplifications were made in the development of these nomograms in order to make them easy to use. For example, a number of assumptions were made to force the prediction of a maximum rate of release. This may or may not represent a "worst-case situation" for some accidents. A slow emission rate for a very toxic substance may necessitate the evacuation of a large area for the entire leak period. A model which is forced to generate maximum release rates falsely predicts a much shorter hazard period.

The objective of this study was to improve the existing nomograms by using more rigorous assumptions and equations for the transfer processes involved (heat, fluid and mass). The system of equations was used to develop a model on a micro-computer (IBM-PC) to permit rapid solution of the iterative balance equations and thus reduce the number of simplifying (and often misleading) assumptions required. Only five representative chemicals are presently included in the model, though others can be easily added. A computer program listing may be found in the report; diskettes are available from Merv Fingas at Environment Canada.

DESCRIPTION OF MODEL

In order to more fully approximate the real physical situation existing after the rupture of a storage or transportation tank containing chemicals, several sub-models were developed and then linked in the computer program. These sub-models include:

- a menu driven routine to select the spilled chemical and specify the seven parameters necessary to fully describe its physical, chemical and thermodynamic properties over the ranges of pressure and temperature,
- an input program to read in the various environmental parameters required,
- a menu driven program to select the type of tank involved and its orientation and calculate the geometric relationships between volume, height of liquid/vapour and heat transfer area
- a menu driven program to select the type, location and orientation of the rupture and to specify the fluid dynamics of the rupture
- a physical/chemical/thermodynamic properties model to calculate, based on the chemical selected and the environmental conditions, the required properties for the heat transfer, mass transfer and fluid dynamics models
- three rupture fluid discharge models, one to describe the release of a compressed gas, one to describe the release of liquid from a hole (including two-phase flow) and one to describe the release of vapour from a rupture above a boiling liquid
- a heat transfer model to calculate the temperature of the tank contents as a function of environmental conditions, tank properties and rate of evaporation of the liquid phase
- three mass balance models; one to calculate pressure drops for leaks in gas tanks, one to predict two-phase flow qualities and one to predict evaporation rates under depressurization conditions

The components of each of these sub-models is described below. The linking of the sub-models to form the computer program is described at the end of this section.

CHEMICAL SELECTION

The model contains five specified chemicals representative of those normally stored and transported in Canada. These are; chlorine, benzene, hydrogen sulphide, anhydrous ammonia and sulphuric acid (66° Be).

The values of the seven parameters which are sufficient to fully describe the physical, chemical and thermodynamic properties of each of the chemicals are stored in this routine. A list of these parameters is given in Table 1.

ENVIRONMENTAL DATA

The following environmental data are required for the various sub-models:

- T_{air} - air temperature (^oK)
- P_{atm} - atmospheric pressure (N/m^2)
- v_{wind} - wind speed (m/s)

TANK SPECIFICATIONS

In order that the model be as flexible as possible, a wide range of tank sizes, orientations and insulation may be specified. From this and a calculation of the initial height of the liquid (or pressure in the case of a compressed gas), the relationship between outflow rate, liquid level (or pressure for a gas), amount of chemical remaining and heat transfer area can be determined and calculated. Four basic tank types can be specified, rectangular, spherical, or cylindrical (oriented either vertically or horizontally). The dimensional relationships for each of these tank types is given in Table 2. Tank wall thickness, insulation thickness and insulation losses are also input here.

RUPTURE SPECIFICATIONS

The rupture in the tank is defined by a shape (circular or rectangular), dimensions, orientation (horizontal or vertical), edge condition (smooth, uniform petals jagged in or out, random petals jagged in), and location (vertical distance from tank bottom to rupture centreline). The coefficient of discharge for liquid or two phase flow through each type of rupture has been taken from Dodge et al, 1980. The values are shown in Table 3. For gas or vapour flow the discharge coefficient is set at 0.61.

TABLE 1

CRITICAL CONSTANTS FOR SELECT CHEMICALS

CHEMICAL	BOILING POINT (^oK)	CRITICAL TEMPERATURE (^oK)	CRITICAL PRESSURE (N/m^2)	MOLECULAR WEIGHT	A*	B* ($x10^3$)	C* ($x10^6$)
CHLORINE	238.4	417	77.1×10^5	70.91	7.576	2.424	-0.965
BENZENE	353.1	561.5	48.3×10^5	78.11	-0.409	77.621	-26.429
HYDROGEN SULPHIDE	213.4	373.4	90.1×10^5	34.08	6.662	5.134	-0.854
AMMONIA	239.6	405.4	113.0×10^5	17.03	6.086	8.812	-1.506
SULPHURIC ACID	563	N/A$^+$	N/A	116.09	N/A	N/A	N/A

* constants required to calculate heat capacity of gases or vapours

+ not available

TABLE 2

TANK GEOMETRY FORMULAE

TANK TYPE	TANK VOLUME, V_T (m^3)	LIQUID VOLUME, V_L (m^3)	HEAT TRANSFER AREA A_{SA} (m^2)	LIQUID/VAPOUR INTERFACIAL AREA A_{SC} (m^2)	HEIGHT OF LIQUID h_L (m)
RECTANGULAR	LWh_T	LWh_L	$2LH_L + 2hW + LW$	LW	V_L/LW
SPHERICAL	$\frac{4}{3}\pi r^3$	$\frac{\pi}{3} h_L{}^2(3r-h_L)$	$2\pi(2r^2-rd)$	$\pi(2rh_L-h_L^2)$	iterative solution
CYLINDRICAL					
-VERTICAL	$\pi r^2 h_t$	$\pi r^2 h_L$	$\pi(2rh_L + r^2)$	πr^2	$V_L/\pi r^2$
-HORIZONTAL	$\pi r^2 L$	$\frac{Lr^2}{2}(\theta - \sin\theta)$	$2\pi(rL + r^2)$	$2L(2rh_L - h_L^2)^{1/2}$	iterative solution

where L = horizontal length of tank (m)
h_T = vertical height of tank (m)
W = width of tank (m)
r = radius of tank (m)
d = depth of penetration of spherical tank into ground (m)
θ = $2\cos^{-1}(1-h_L/r)$

TABLE 3
DISCHARGE COEFFICIENTS FOR LIQUID OR TWO-PHASE FLOW

RUPTURE SHAPE	EDGE* CONDITION	ORIENTATION	DISCHARGE COEFFICIENT
Circular	Smooth	---	0.65
Circular	UPJI	---	0.622
Circular	RPJI	---	0.577
Rectangular	Smooth	Horizontal	0.619
Rectangular	Smooth	Vertical	0.625
Rectangular	UPJI	Horizontal	0.629
Rectangular	UPJI	Vertical	0.626
Rectangular	RPJI	Horizontal	0.609
Rectangular	RPJI	Vertical	0.613
Rectangular	UPJO	Horizontal	0.826
Rectangular	UPJO	Vertical	0.828

* UPJI = Uniform Petals Jagged In
UPJO = Uniform Petals Jagged Out
RPJI = Random Petals Jagged In

source: Dodge et al, 1980

CHEMICAL PROPERTIES

Gaseous State

The basis for the calculation of the chemical properties for the gaseous state is the Redlich-Kwong equation of state (Redlich & Kwong, 1949):

$$P\underline{V} = ZRT \quad (1)$$

$$Z = (1/(1-[b/\underline{V}])\text{)}-(a/RT^{3/2}\underline{V}[1+(b/\underline{V})]) \quad (2)$$

and

$$a = 0.4278\ R^2T_C^{5/2} \quad (3)$$

$$b = 0.0867\ RT_C/P_C \quad (4)$$

where P = pressure (N/m^2)
$\underline{V}$ = molar volume (m^3/kg mole)
Z = compressibility factor
R = 8.314×10^3 (J/kg mole ^{o}K)
T = temperature (^{o}K)
T_C = critical temperature (^{o}K)

Gas Density. The gas (or vapour) density is calculated using an iterative procedure. Given an initial pressure and temperature an initial guess of molar volume is calculated from:

$$\underline{V}_i = RT/P \quad (5)$$

The value of Z is then calculated using equations 2, 3 and 4 and the next value of molar volume is calculated by:

$$\underline{V}_{i+1} = Z\ RT/P \quad (6)$$

The process is repeated until two consecutive values of V are less than 1% apart. The vapour density is then given by:

$$\rho_V = M.W./\underline{V}_{i+1} \quad (7)$$

where ρ_V = vapour density (kg/m^3)
M.W. = molecular weight of chemical (kg/kg mole)

Gas Heat Capacity and Ratio. The heat capacity at constant pressure is calculated from (Balzhizer et al, 1972);

$$Cp_g = 4.184 \times 10^3 (A+BT+CT^2)/M.W. \quad (8)$$

where Cp_g = heat capacity at constant pressure of 1 atm. (J/kg ^{o}K)
A,B,C, = constants for each chemical (see Table 1)

The heat capacity is adjusted for pressure by (Perry & Chilton, 1973);

$$\Delta C_{Pg} = 4.184x10^3(T_R/1.686)^{-3.72}P_R^{0.9155}/M.W. \qquad (9)$$

where ΔC_{Pg} = correction added to C_{Pg} to account for different pressure (J/kg °K)
T_R = reduced temperature
= T/T_C
P_R = reduced pressure
= P/P_C

The ratio of heat capacity at constant pressure to heat capacity at constant volume (C_{vg}) is given by (Perry & Chilton, 1975);

$$k = C_{Pg}/(C_{Pg}-[8.314x10^3/M.W.]) \qquad (10)$$

Liquid State

Liquid Density. Bhirud's method is used to calculate the liquid density (Lyman et al, 1982);

$$\rho_L = 10^3 M.W.P_C/RT\ e^{(a+wb)} \qquad (11)$$

and,

$$a = 1.396444-24.07T_R+102.615T_R^2- 255.719T_R^3+355.806T_R^4- 256.671T_R^5+75.1088T_R^6 \qquad (12)$$

$$b = 13.4412-135.7437T_R+533.380T_R^2- 1091.453T_R^3+1231.43T_R^4 -728.227T_R^5+176.737T_R^6 \qquad (13)$$

$$w = \frac{3}{7}(T_{BR}/[1-T_{BR}])\ (\log(P_C/1.01x10^5)-1)$$

where ρ_L = liquid density (kg/m^3)
a,b = constants
w = accentric factor
T_{BR} = reduced boiling point
= T_B/T_R
T_B = boiling point (°K)

Liquid Heat Capacity. The heat capacity at constant pressure is calculated from the gas heat capacity at constant pressure by (Perry & Chilton, 1973);

$$C_{Pl} = C_{Pg}+(4.686x10^4/M.W.) \qquad (14)$$

where C_{Pl} = liquid heat capacity at constant pressure (J/kg°K)

Heat of Vaporization. The Reidel equation (Lyman et al, 1982) is used to estimate the heat of vaporization at the boiling point;

$$\Delta H_{VB} = \frac{4.184\text{x}10^{3}T_{B}(5\log[P_{C}/1.01\text{x}10^{5}]-2.17)}{M.W.\,(0.930-T_{BR})} \qquad (15)$$

where ΔH_{VB} = heat of vaporization at the normal boiling point (J/kg)

This value is corrected for temperatures other than the normal boiling point using an adaption of the Thiesen correlation (Lyman et al, 1982);

$$\Delta H_{V} = \Delta H_{VB}([1-T_{R}]/[1-T_{BR}])^{0.38} \qquad (16)$$

Surface Tension. The liquid surface tension at the boiling point (it's only use in the model) is calculated using Walden's rule (Perry & Chilton, 1973);

$$\sigma = 6.56\text{x}10^{7}\Delta H_{VB}\,\rho_{L} \qquad (16A)$$

where σ = surface tension (N/m)

Kinematic Viscosity Ratio. The ratio of liquid to gas kinematic viscosity is determined by dividing Arrhenuis's relation for liquid viscosity by Arnold's correlation for gas viscosity (both converted from dynamic to kinematic terms) to yield;

$$\nu_{L}/\nu_{V} = 37M.W.^{1/6}\rho_{V}(T+1.47T_{B})/\rho_{L}^{\;7/6}T^{3/2} \qquad (17)$$

where ν_{L}/ν_{V} = ratio of liquid to gas kinematic viscosity

Vapour Pressure. The vapour pressure of the liquid is calculated using Riedel's analytical correlation (Perry & Chilton, 1973);

$$P_{V} = P_{C}/10^{(0.118B-7\log T_{R}+[\alpha_{C}-7][0.0364B-\log T_{R}])} \qquad (17A)$$

and

$$B = (36/T_{R})-35-T_{R}^{\,6}+42\ln T_{R} \qquad (17B)$$

$$\alpha_{C} = 0.9076(1+[T_{BR}\ln[P_{C}/1.01\text{x}10^{5}]]/[1-T_{BR}]) \qquad (17C)$$

GAS FLOW THROUGH RUPTURE

If the contents of the tank are gaseous (or only vapour is present) at elevated pressure the outflow rate is calculated as follows;

- first, the initial tank pressure is determined using the equation of state (equation 1) and:

  $$\underline{V} = V_{T}M.W./CMASS \qquad (18)$$

  where CMASS = mass of chemical in tank (kg)

- next, a series of calculations are performed to determine whether or not the flow is sonic or subsonic:

$\beta = D_R/D_T$ (19)

where D_R = diameter of rupture (m)
= $2r_R$, for circular holes
= $(L_R W_R)^{1/2}$, for rectangular holes

D_T = diameter of tank
= 2r for cylindrical or spherical tanks
= $(LWh)^{1/3}$ for rectangular tanks

if $\beta < 0.2$

$r_c = (2/[k+1])^{k/(k-1)}$ (20)

where r_c = critical pressure ratio for sonic flow

if $\beta > 0.2$

$r_c^{(1-k)/k} + (k-1)\beta^4 r_c^{(2/k)}/2 = (k+1)/2$ (21)

if $r_c \geq P_{atm}/P_{tank}$ sonic flow exists
if $r_c < P_{atm}/P_{tank}$ sub-sonic flow exists

where P_{atm} = atmospheric pressure (N/m^2)
P_{tank} = pressure in tank (N/m^2)

- The mass flow rate through the rupture is then determined by the appropriate sonic or sub-sonic flow equation.

Sonic Flow

$\dot{m} = C_D A_R (k(P_T \rho_V)(2/[k+1])^{(k+1)/(k-1)})^{1/2}$ (22)

where C_D = discharge coefficient
= 0.61

A_R = area of rupture (m^2)
= πr^2 for circular hole
= $L_R W_R$ for rectangular hole

$\dot{m}$ = mass flow through rupture (kg/s)

If the flow is initially sonic, the model calculates the mass flow for twenty uniform iterations from the initial tank pressure to the pressure at which subsonic flow commences.

Subsonic Flow

Assuming isentropic flow:

$\dot{m} = C_D A_R Y(2(P_{tank} - P_{atm})\rho_V)^{1/2}/(1-\beta^4)^{1/2}$ (23)

and

$Y = 1-([1-r]/k)(0.41+0.35\beta^4)$ (24)

where Y = expansion coefficient
r = pressure ratio
= P_{atm}/P_{tank}

The model then calculates the mass flow for twenty uniform iterations from the initial tank pressure (or from the pressure at which the flow becomes subsonic - see above) to atmospheric pressure.

No heat transfer calculations are required for either the sonic or subsonic gas flow model since the gas cools only as it expands isentropically through the rupture.

LIQUID FLOW THROUGH RUPTURE

For the case of a liquid whose vapour pressure is less than atmospheric pressure (i.e., its boiling point is above the ambient temperature) the flow through the rupture is incompressible and can be calculated from (Dodge et al, 1980).

$$\dot{m} = C_D A_R (2P_{hole} - P_{atm}) \rho_L)^{1/2} / (1-\beta^4)^{1/2} \qquad (25)$$

and

$$P_{hole} = (h_L - h_R + D_R/2) \rho_L g + P_v \qquad (26)$$

where P_{hole} = pressure in liquid at rupture centreline (N/m^2)
g = acceleration of gravity (9.81 m/s^2)

The model calculates the liquid outlfow for increments of 5 cm drops in liquid level until either the pressure at the hole drops close to atmospheric pressure and air is ingested into the tank or the liquid level reaches the top of the hole. Once the latter occurs P_v is set at atmospheric pressure and the calculations continue in 5 cm increments until the bottom of the hole is reached, at which time the flow stops.

Air Ingestion

It is well known that once the pressure difference across the rupture approaches zero, air will be ingested into the tank and an equivalent volume of chemical flow out. This is accounted for in the model by using a variation of the approach proposed by Dodge et al, 1980. Once $P_{hole} \leq 1.01\ P_{atm}$, air ingestion begins at a volumetric rate equal to the liquid outflow which is equal to the mass flow from equation 25 with P_{hole} set at 1.01 P_{atm}. This continues in 5 cm increments of liquid level until the height of the liquid equals the height of the top of the hole. At this point P_v is set equal to P_{atm} and the model reverts to equations 25 and 26. This continues in 5 cm increments until the liquid level reaches the bottom of the hole and flow stops.

Evaporation Losses

Once the liquid level in the tank begins to drop the pressure in the vapour space falls. If this continues to a point where the pressure drops below the vapour pressure of the chemical evaporation of the liquid in the tank will begin. This is accounted for by (Dodge et al, 1980):

$$\dot{m}_e = \dot{m}_{esat'd} - (1.9(\dot{m}_{esat'd})^{5/4}/(\rho_L A_{SC}(RT)^{1/2})^{1/4}) \qquad (27)$$

and

$$\dot{m}_{esat'd} = \rho_v \dot{m}/(\rho_L - \rho_v) \qquad (28)$$

where $\dot{m}_e$ = mass evaporation rate of liquid into vapour space (kg/s)

$m_{esat'd}$ = theoretical equilibrium evaporation rate (kg/s) to fill vapour space as liquid level falls

The time required to discharge 5 cm of the liquid is then reduced by an amount proportional to the evaporation rate.

The evaporation process sets up a heat flow into the tank. This is discussed in the next section dealing with two-phase flow.

TWO-PHASE FLOW THROUGH RUPTURE

For liquids whose vapour pressure is greater than atmospheric pressure two situations can result in two-phase flow through the rupture. The first of these is flow through a hole below the liquid level at a rate sufficient to cause boiling of the liquid as the vapour space pressure decreases. The second is boiling and subsequent overflow caused by rapid depressurization of the vapour space from a hole above the liquid level. Both situations are extremely complex since heat tranfer, mass transfer and two-phase flow are occurring simultaneously.

Void Fraction

The most important factor in the two-phase flow model is the volumetric void fraction of vapour in the liquid (or its mass equivalent; quality). The void fraction, or "holdup", in a flashing liquid (due to depressurization) is calculated using Viecenz's experimental correlation (Mayinger, 1981):

$$\varepsilon = 0.73(U_{og}^{2}/g(\sigma/g(\rho_L-\rho_v))^{1/2})^{0.376}((\sigma/g(\rho_L-\rho_v))^{1/2}/D_{tank})^{0.176}(\rho_L/(\rho_L-\rho_v))^{0.585}(\text{[illegible]})^{0.256} \qquad (29)$$

in which

$$U_{og} = \dot{m}e/\rho_v A_{sc} \qquad (30)$$

where ε = void fraction
U_{og} = superficial vapour velocity (m/s)

The stagnation quality is related to void fraction through:

$$X_o = \rho_v/(\rho_v+((1/\varepsilon)-1)+\rho_L) \qquad (31)$$

where X_o = stagnation quality or the mass fraction of vapour in the fluid

The presence of vapour bubbles in the tank creates an expansion in the fluid volume necessitating a redefinition of liquid height; one, the actual fluid level in the tank including vapour bubbles (h_L) and another an equivalent height of liquid if no bubbles were present (h_{LE}) which is used for pressure calculations. The fluid volumes which, in combination with tank geometry calculations, are used to determine h_L and h_{LE} are related by:

$$V_L = V_{LE}/(1-\varepsilon) \qquad (32)$$

Hole Below Liquid Level

Two-Phase Subsonic Flow. If the void fraction is greater than 0.01 the flow is considered two-phase and choking can occur (sonic flow). The critical pressure ratio is determined from (Henry, 1981)

$$r_c = e^{(-0.4353X_o-0.1625)} \qquad (33)$$

If r_c P_{atm}/P_{hole} the flow is subsonic. The mass flowrate is calculated by (Delhaye, 1981):

$$\dot{m} = C_D A_R Y(2(P_{hole}-P_{atm})/(X_o^{1.5}((1/\rho_v)-(1/\rho_L))+(1/\rho_L)))^{1/2}/(1-\beta^4)^{1/2} \qquad (34)$$

In which Y, the expansion coefficient of the vapour is calculated as in the gas model (equation 24). Note that if X_o is 0, equation 34 becomes equation 25 with Y=1 for one phase incompressible flow. If X_o=1, equation 34 becomes equation 23 for one phase compressible flow.

Two-Phase Sonic Flow. If $r_c \leq P_{atm}/P_{hole}$ then the flow is sonic. The mass flowrate is given by (Henry, 1981):

$$\dot{m} = \frac{C_D A_R Y}{(1-\beta^4)^{1/2}}\left(2\rho_L P_{hole}(1-\varepsilon)\frac{(((1-\varepsilon)/\varepsilon)(1-r_c)+((k/(k-1))(1-r_c^{((k-1)/k)})))}{(1-X_o)\varepsilon(((1-\varepsilon)/\varepsilon)+r_c^{(-1/k)})^2}\right)^{1/2} \qquad (35)$$

As X_o and ε approach 1 equation 35 approaches equation 22 for one phase compressible critical flow.

Hole in Vapour Space

In the event of a hole in the vapour space the model starts by using the gas model (Section 2.6) for either sonic (equation 22) or subsonic (equation 23) flowrate.

As the pressure in the vapour space decreases, the liquid boils (equations 27 and 28), a fraction of vapour is held up in the liquid (equation 29 and 30) and the fluid expands (equation 32).

If the height of the flashing fluid reaches the rupture, the model calculates the outflow rate on the basis of either sonic (equation 35) or subsonic (equation 34) flow. At this point the rate of pressure loss due to vapour outflow is reduced by liquid flowing from the rupture, the vapour space pressure increases by vapour generation from the flashing liquid, the void fraction decreases, the fluid volume decreases and the liquid level drops below the rupture. The model then reverts to the gas flow equations and the process is repeated. This continues until the flashing liquid level no longer reaches the rupture, either because of fluid losses or evaporative cooling (combined with heat transfer - see below) at which point the driving force for the outflow is the vapour pressure of the chemical. Once the temperature of the liquid reaches its boiling point (ie the vapour pressure equals atmospheric pressure) the mass loss rate is equal to the evaporation rate as determined by heat transfer.

All the two-phase flow models use 5 cm increments in liquid level for determining flowrates.

HEAT TRANSFER

The key heat transfer process involved in the release of liquid chemicals from a rupture is cooling of the bulk liquid through evaporation (heat of vaporization and heat capacity of the chemical) combined with warming of the liquid by heat transferred from the environment through the tank walls. The balance of these two heat flows defines the temperature of the liquid and vapour (and thus their physical, chemical and thermodynamic properties) and the final rate at which low boiling liquids are released through ruptures in the vapour space.

The equation for determining the temperaure of the tank contents is:

$$T_{i+1} = T_i - ((\dot{m}_e \Delta H_v \Delta t_i) - (U_o A_S \Delta t_i (T_{air} - T_i)))/\rho_L V_{Li} C_{pl} \qquad (36)$$

where T_i, T_{i+1} = temperature of liquid in tank before and after each iteration (^oK)

Δt_i = calculated time of outflow for each iteration (s)

U_o = overall heat transfer coefficient ($J/sm^2 {}^oK$)

T_{air} = air temperature (^oK)

The overall heat transfer coefficient is determined as shown below.

Overall Heat Transfer Coefficient

$$U_o = 1/((1/h_i)+(x_w/k_w)+(x_I/k_I)+(1/h_o)) \qquad (37)$$

where h_i,h_o = inside and outside heat transfer coefficeints (J/m^2s^oK)

x_w,x_i = wall and insulation thickness (m) x_w is input or set at 0.01 m; xI is arbitrarily set at either 0 or 0.1 m

K_w,K_i = wall and insulation thermal conductivities (J/ms^oK) K_w = 16.45 J/ms^oK (steel); K_i = $2.74x10^{-3}$ J/ms^oK (average for foam)

Outside Heat Transfer Coefficient

The outside heat transfer coefficient is calculated by (Perry & Chilton, 1973):

$$h_o = 0.017B(6.67x10^4Lv_{wind})^n/L \qquad (38)$$

where v_{wind} = wind speed (m/s)

L = tank dimension (m) - see below

B,n = constants defined by tank shape as shown in Table 4

TABLE 4

OUTSIDE HEAT TRANSFER COEFFICIENT CONSTANTS

TANK SHAPE	PARAMETER IN EQUATION 38		
	L	B	n
cylindrical	diameter	0.0266	0.805
spherical	diameter	0.6	0.5
rectangular	shortest dimension	0.104	0.675

Inside Heat Transfer Coefficient

The inside heat transfer coefficient is determined from one of two equations, depending on whether or not the liquid is boiling (Perry and Chilton, 1973);

for $T_i <$ boiling point

$$h_i = 69\Delta T_{wall}{}^{1/4}/h_L{}^{1/4} \qquad (39)$$

where $\Delta T_{wall} = (T_{wall}-T_{air})$
T_{wall} = inside tank wall temperature (°K)

Calculation of h_i requires an iterative procedure in which the first guess at T_{wall} is:

$$\Delta T_{wall_i} = (T_{air}-T_i)/2 \qquad (40)$$

h_i, h_o and U_o are then calculated and the next guess at ΔT_{wall} is:

$$\Delta T_{wall_{i+1}} = U_o \ (T_{air}-T_i)/h_i \qquad (41)$$

The process continues until two successive iterations are within 2.5% of each other.

for $T_i > T_{boil}$

$$h_i = 3x10^{-6}P_C\ 1.69\ P_R\ 0.35(1-P_R)0.9(1.8P_R{}^{0.17}+4P_R{}^{1.2}+10P_R{}^{10}) \qquad (42)$$

Insulation Losses

If an area of insulation around the rupture is destroyed the overall heat transfer coefficient is modified by summing the contributions to the total heat transfer of the insulated and uninsulated aeas:

$$U_o = U_o^{I}(1-(A_{ID}/A_{SA}))+U_o^{II}(A_{ID}/A_{SA}) \qquad (43)$$

where A_{ID} = arca of insulation destroyed (m^2)
$U_o{}^{I}$ = overall heat transfer coefficient including insulation (J/m^2s^oK)
$U_o{}^{II}$ = overall heat transfer coefficient excluding insulation (J/m^2s^oK)

COMPUTER PROGRAM DESIGN

The general computer program structure, that integrates the equations presented in Section 2.0 is outlined in the following four flow charts (See Figures 1 to 4). A brief description of the workings of the model, based on these flowcharts follows. A complete program listing may be found in the report.

MAINLINE PROGRAM STRUCTURE - "LEAKR"

The mainline program "LEAKR" controls the flow of the model by calling up the appropriate data imput and data manipulation routines. As is illustated in Figure 1, the chemical selection sub-routine "CHEM" is called which prompts the user to identify the chemical spilled and its initial temperature. The routine also supplies the mainline program with the 7 chemical characteristics required to calculate the chemical's physical and chemical properties as a function of temperature and pressure. Control is then passed to the environmental data imput sub-routine "ENVCON" which prompts the user for the air temperature, atmospheric pressure and wind speed at the spill site. The next routine called is the tank geometry input model "TANKG". The tank shape, wall thickness, insulation thickness, area of damaged insulation, and tank dimensions are all input at this stage in the program. Sub-routine "RUPTURE" is then called which prompts the user to select the rupture type (out of a possible 12) and enter the rupture size and location. The routine then selects the coefficient of discharge based on the puncture type selected. At this point the chemical properties needed in the discharge equations are initialized by calling sub-routine "INIT". "INIT" asks the user for the mass of chemical present in the tank and then calls upon either the "LEQNS" or "GEQNS" sub-routine to determine the initial chemical properties for the Liquid or Gas which is present. This routine then prints a listing of these initial chemical properties prior to carrying on. At this stage in "LEAKR" a check is made to determine which outflow model should be used to calculate the chemical discharge rate. If the chemical is present as a gas only control is transferred to the GAS model. All of the chemical is discharged via this model and the calculations are complete. Details of the GAS model are discussed in a following section. If the chemical is present as a liquid a check is made on the liquid level to see if it is above the "hole" bottom. If it is, transfer is passed to the liquid model, "LIQMOD", which handles the discharge of the chemical until the liquid level drops below the bottom of the hole. Details of this model can be found in Section 3.3. At this time a check is made to see if the chemicals vapour pressure is greater than atmospheric pressure. If it is not no more chemical will escape and the program terminates. This same check also occurs if the liquid level is initially below the bottom of the hole. If the vapour pressure (VAPP) is greater then atmospheric pressure control is passed to the vapour discharge model, "VAPMOD". Chemical escapes from the tank by boiling off from the liquid pool and escaping as vapour. If during this boiling the liquid level rises above the hole's bottom control is passed to the liquid model which discharges chemical until the liquid level again drops below the hole bottom. When all of the liquid is boiled off a check is made to see if the tank pressure is greater then atmospheric pressure. If it is, control is passed to the GAS model to discharge the remaining vapours in the tank. If the pressure is less than amospheric the program is terminated. The detailed workings of the GAS, LIQUID and VAPOUR models follow.

GAS DISCHARGED MODEL - "GASMOD"

When control is passed to the gas model an initial check is made to determine if the discharge is sonic or sub-sonic. The appropriate discharge equation is selected to determine the mass flow rate at the existing tank pressure. This mass flow rate is assumed to take place until the pressure drops a pre-determined amount. The new chemical properties are calculated at this new pressure. Knowing the gas density at the old and new pressure then allows the calculation of the amount of chemical lost during the pressure drop. The time to release this mass of chemical is then calculated using the mass flow rate at the initial pressure and the total mass lost. Finally a check is made to determine if sonic or sub-sonic flow exists. If the flow is sonic the process is repeated until sub-sonic flow exists; if the flow is sub-sonic the process is repeated until the tank pressure falls below atmospheric and the routine ends. If the flow is initially sonic 20 iterations of the sonic discharge equation (in 20 uniform pressure drops) are completed to bring the discharge to a sub-sonic condition. Once the flow is sub-sonic 20 terations of the sub-sonic equation are carried out (again in 20 equal pressure drops) to discharge the remaining mass of chemical (atmospheric pressure is reached in the tank).

LIQUID DISCHARGE MODEL - "LIQMOD"

The first step in the liquid discharge model is the calculation of pressure at the puncture centre (tank pressure + head of liquid over hole). If the pressure is greater than 1.01 x atmospheric pressure liquid will flow out. If it is not air is ingested (@ Patm) until the pressure increases to allow the liquid to flow. At this point the program checks for a two-phase flow condition. If this does not exist the simple liquid discharge model is implemented to calculate the mass outflow rate. If two-phase flow exists a check is made to determine if it is sonic or sub-sonic and the routine branches to the appropriate mass flow rate equation to calculate this mass flow rate. After the calculation of the mass flow rate the liquid level is dropped by a uniform amount (0.05 metre was used in the model) and the volume of liquid the function lost by the drop in liquid level is calculated by determining the new liquid volume (using the function sub-routine "VOL") and subtracting from the old volume. The new tank pressure is then calculated by a simple ideal gas relationship. The time to lose this volume of liquid is then determined by dividing the total mass of liquid lost by the mass flow rate plus the evaporation rate. This then accounts for the fact that some of the liquid is simply lost to the vapour space and is not actually discharged from the tank. The new tank temperature is calculated by first reducing its temperature due to evaporative heat loss (based on the evaporation rate) and then by calling the heat transfer routine "TEMP" to adjust the temperature of the tank due to heat loss/gain to the surrounding environment. The new chemical properties are then calculated using the sub-routine "LEQNS". If the flow is two-phase the height of the boiling liquid is calculated and then a check is made to see if the liquid is still above the top of the hole. If it is the process is started again with the calculation of the pressure at the rupture centre. If it is not above the top of the hole a check is made to see if it is above the bottom of the hole. If it is the vapour pressure is checked against the prevailing atmospheric pressure and the larger of the two is assigned to this tank pressure. If the liquid level drops below the hole the vapour pressure is again compared to atmospheric. If it is less than equal to atmospheric the program ends as no more chemicl will be discharged. If the vapour presure is greater than Patm and there is still liquid in the tank control is passed to the vapour model to discharge the remaining liquid. If there is no liquid left control is passed back to the main line routine where the remaining chemical will be discharged using the gas model, "GASMOD".

VAPOUR RELEASE MODEL - "VAPMOD"

Upon entering the "VAPMOD" routine the mass flow rate is calculated for the existing temperature and pressure conditions (the appropriate sonic or sub-sonic operations are used. If the liquid boils violently to fill the tank (or raise the liquid level above the bottom of the puncture) control is passed back to the liquid model after adjusting the tank temperature, due to the evaporative heat losses, and calculating the new chemical properties. If the liquid does not boil above the hole a check is made on the tank's temperature. If the temperature of the chemical is less than or equal to its boiling temperature the mass outflow is then controlled only by the heat transfer into the tank. The time to discharge the remaining chemical is then calculated in one step and the program ends. If the temperature of the chemical is above its boiling point the routine continues. The liquid level is adjusted by DH (0.05 metres) and the volume of liquid lost is again determined by the function sub-routine "VOL". The time to lose the chemical is calculated by dividing the mass of liquid lost by the evaporation rate (which in turn is a function of the mass flow rate out of the puncture). The evaporation rate is used here because the only way the liquid level can drop is by evaporation. If there is liquid remaining in the tank the new tank temperature is calculated using the heat transfer routine and the evaporative heat losses. The new tank pressure is calculated and finally the chemical properties are re-evaluated. The routine is then repeated.

MODEL RESULTS

Unfortunately suitable field or laboratory data could not be found in the literature to allow validation of the model's output. The accuracy of the model is therefore unknown.

Nomographs similar to those presented in the TIPS manuals have been prepared for Ammonia, Chlorine, Benzene and Hydrogen Sulphide. These graphs are presented as Figures 5 to 11. It was not possible to run the model for Sulphuric Acid as several of the required constants were not available. Also included on each of these figures are the original TIPS leak rate predictions. The following can be said about the comparison of the two sets of results:

i) For benzene, the chemical with the lowest vapour pressure, the discharge from a hole in the bottom of a tank car predicted by the new model was slower than that from the original TIPS results for all rupture sizes. See Figure 5.

ii) For the remaining chemicals, all low boiling point liquids with high vapour pressures, the new model predicted a faster release of chemical for punctures in the tank bottom except for the smallest hole size (50 mm) where the results were very similar to those in the EnviroTIPS Manuals.

It should be noted that these differences in release rate predictions (for high vapour pressure chemicals and holes in the bottom of tank cars) are not really significant from a countermeasures or safety point of view, since the total release times predicted by the two methods lie between about 0.1 to 10 minutes.

iii) A major difference between the EnviroTIPS results and the new model's predictions arises when a comparison is made of the results for holes in the top of the tank car. Because of the heat transfer component in the new model its discharge predictions are much slower than the TIPS results. The flattening out of the curves for the new predictions is a result of the tank temperature dropping to the boiling point of the liquid at which time the heat transfer controls the evaporation process and therefore the chemical release rate.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1) A simple-to-use computerized model to determine the rate and duration of leaks from chemical storge and transportation tanks has been developed.
2) The model is very flexible, capable of handling a wide range of tank and rupture sizes and shapes.
3) No knowledge of chemical properties (other than name and the amount in the tank) is required to operate the model.
4) Significant differences between the EnviroTIPS predictions and the computer model predictions exist for the cases of a puncture in the vapour space of tanks containing liquefied gases (chemicals with vapour pressures exceeding atmospheric at ambient temperatures).

RECOMMENDATIONS

1) Simple small and meso-scale tests should be carried out to validate the model.
2) The selection of chemicals stored in the program should be extended to include the most commonly spilled materials.
3) Once a generally accepted atmospheric dispersion model is available, the leak rate model should be configured to link with it.
4) Since it is virtually impossible to determine rupture size and shape at the scene of an accident a technique to determine this should be researched.
5) The model should be extended to permit the user to select the output desired (ie duration, maximum flowrate, chemical properties, etc).

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FIGURE 1 MAINLINE PROGRAM STRUCTURE

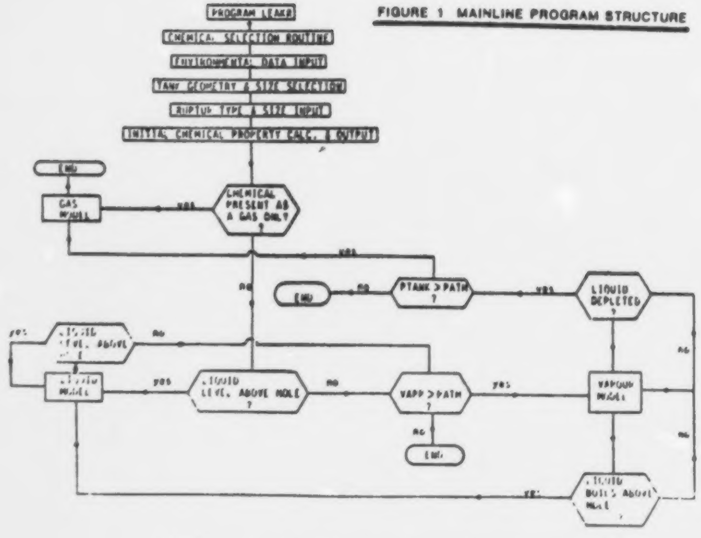
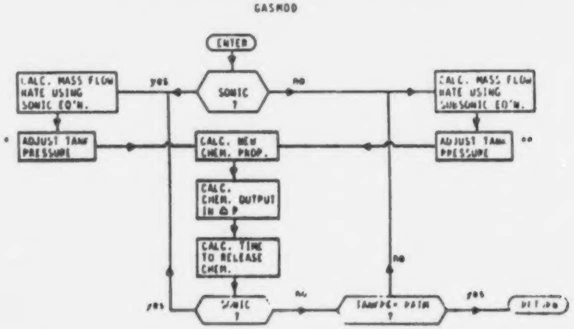

PROGRAM LEAKR
CHEMICAL SELECTION ROUTINE
ENVIRONMENTAL DATA INPUT
TANK GEOMETRY & SIZE SELECTION
RUPTURE TYPE & SIZE INPUT
INITIAL CHEMICAL PROPERTY CALC. & OUTPUT
END
GAS MODEL
yes
CHEMICAL PRESENT AS A GAS ONLY ?
no
yes
END
no
PTANK > PATH ?
yes
LIQUID DEPLETED ?
LIQUID LEVEL ABOVE HOLE ?
LIQUID MODEL
yes
LIQUID LEVEL ABOVE HOLE ?
no
VAPP > PATH ?
yes
VAPOUR MODEL
no
END
LIQUID BOILS ABOVE HOLE ?

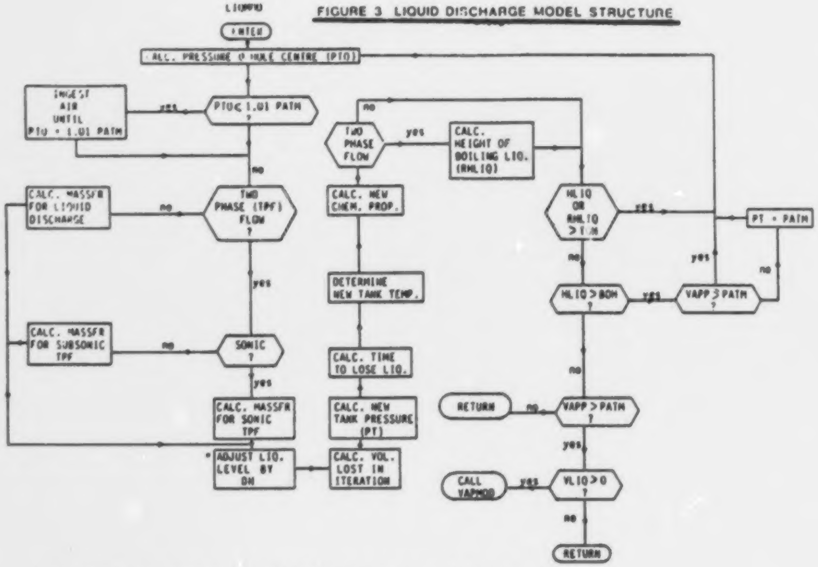
FIGURE 2 GAS DISCHARGE MODEL STRUCTURE


GASMOD
ENTER
CALC. MASS FLOW RATE USING SONIC EQ'N.
yes
SONIC ?
no
CALC. MASS FLOW RATE USING SUBSONIC EQ'N.
*
ADJUST TANK PRESSURE
CALC. NEW CHEM. PROP.
ADJUST TANK PRESSURE
**
CALC. CHEM. OUTPUT IN ΔP
CALC. TIME TO RELEASE CHEM.
no
yes
SONIC ?
no
TANKP<= PATH ?
yes
RETURN

* If flow is sonic the pressure is dropped in 20 uniform iterations until sub-sonic flow is reached. Then control is transferred to the subsonic routine.

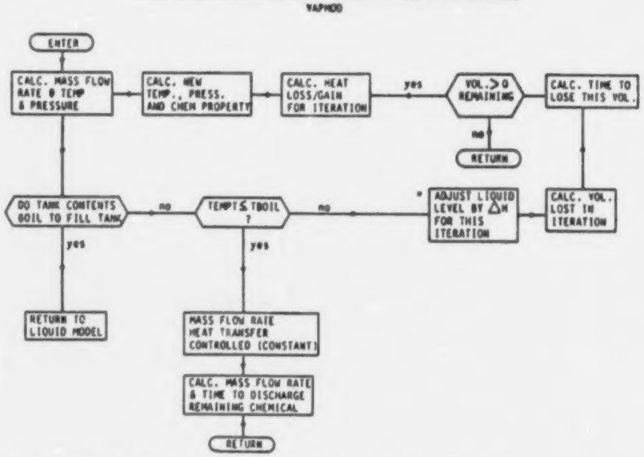
** Once subsonic flow is reached the pressure is dropped in 20 uniform iterations until the tank pressure = atmospheric pressure and discharge ceases.

FIGURE 3 LIQUID DISCHARGE MODEL STRUCTURE


LIQMOD
ENTER
CALC. PRESSURE @ HOLE CENTRE (PTO)
INGEST AIR UNTIL PTO = 1.01 PATH
yes
PTO< 1.01 PATH ?
no
TWO PHASE (TPF) FLOW ?
no
CALC. MASSFR FOR LIQUID DISCHARGE
yes
CALC. MASSFR FOR SUBSONIC TPF
no
SONIC ?
yes
CALC. MASSFR FOR SONIC TPF
* ADJUST LIQ. LEVEL BY DH
CALC. VOL. LOST IN ITERATION
CALC. NEW TANK PRESSURE (PT)
CALC. TIME TO LOSE LIQ.
DETERMINE NEW TANK TEMP.
CALC. NEW CHEM. PROP.
TWO PHASE FLOW
yes
CALC. HEIGHT OF BOILING LIQ. (RHLIQ)
no
HLIQ OR RHLIQ > DH
yes
no
HLIQ > BOH ?
yes
VAPP ≥ PATH ?
yes
no
PT = PATH
no
RETURN
no
VAPP > PATH ?
yes
CALL VAPMOD
yes
VLIQ > 0 ?
no
RETURN

* Model is driven by iterations in liquid level and volumes lost with this change in level

FIGURE 4 VAPOUR DISCHARGE MODEL STRUCTURE


VAPMOD
ENTER
CALC. MASS FLOW RATE @ TEMP & PRESSURE
CALC. NEW TEMP., PRESS. AND CHEM PROPERTY
CALC. HEAT LOSS/GAIN FOR ITERATION
yes
VOL. > 0 REMAINING
CALC. TIME TO LOSE THIS VOL.
no
RETURN
DO TANK CONTENTS BOIL TO FILL TANK
no
TEMPT ≤ TBOIL ?
no
* ADJUST LIQUID LEVEL BY ΔH FOR THIS ITERATION
CALC. VOL. LOST IN ITERATION
yes
yes
RETURN TO LIQUID MODEL
MASS FLOW RATE HEAT TRANSFER CONTROLLED (CONSTANT)
CALC. MASS FLOW RATE & TIME TO DISCHARGE REMAINING CHEMICAL
RETURN

* Note the model is driven by a constant change in liquid level for each iteration and the time it takes to evaporate and discharge this liquid volume

FIGURE 5

BENZENE DISCHARGE NOMOGRAPH - HOLE IN BOTTOM OF RAILWAY TANK CAR

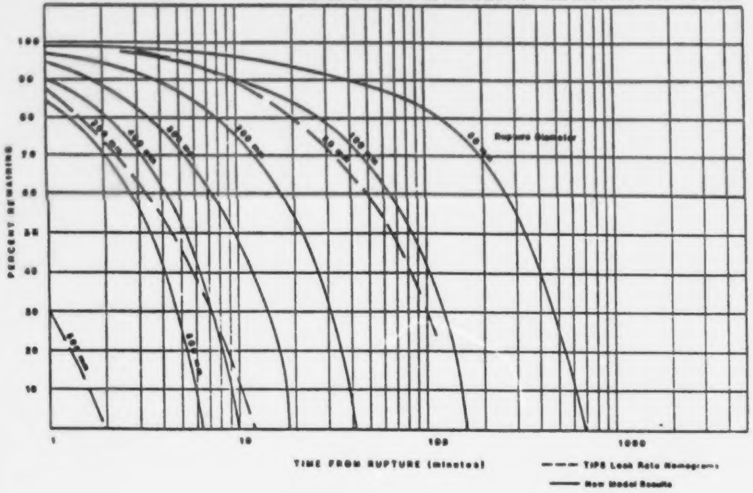


FIGURE 6

CHLORINE DISCHARGE NOMOGRAPH - HOLE IN BOTTOM OF RAILWAY TANK CAR

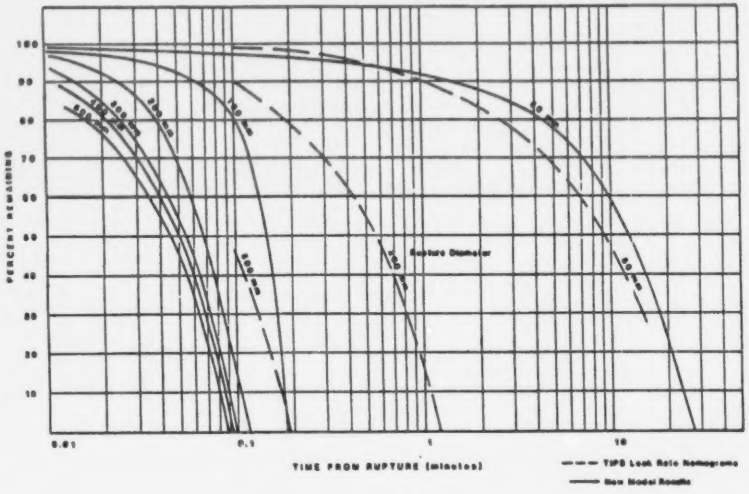


FIGURE 7

CHLORINE DISCHARGE NOMOGRAPH - HOLE IN TOP OF RAILWAY TANK CAR

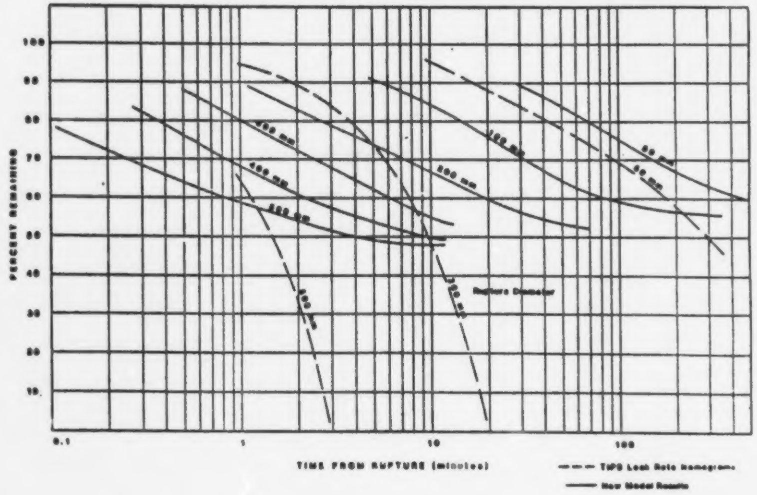


FIGURE 8

AMMONIA DISCHARGE NOMOGRAPH - HOLE IN BOTTOM OF RAILWAY TANK CAR

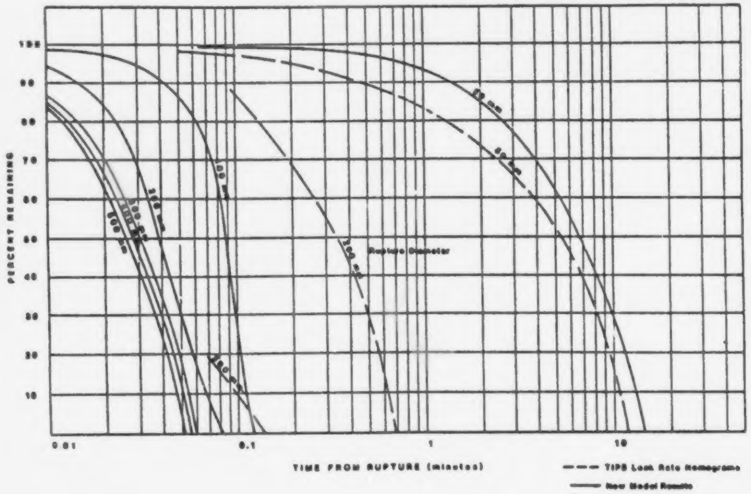


FIGURE 9

AMMONIA DISCHARGE NOMOGRAPH - HOLE IN TOP OF RAILWAY TANK CAR

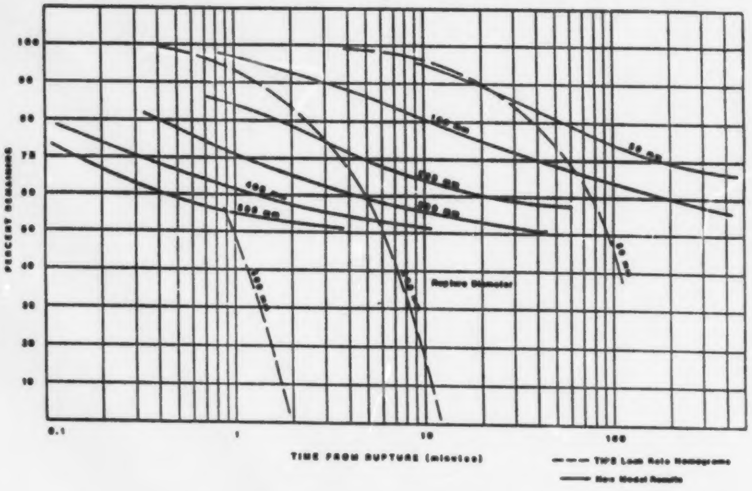


FIGURE 10

HYDROGEN SULPHIDE DISCHARGE NOMOGRAPH - HOLE IN BOTTOM OF RAILWAY TANK CAR

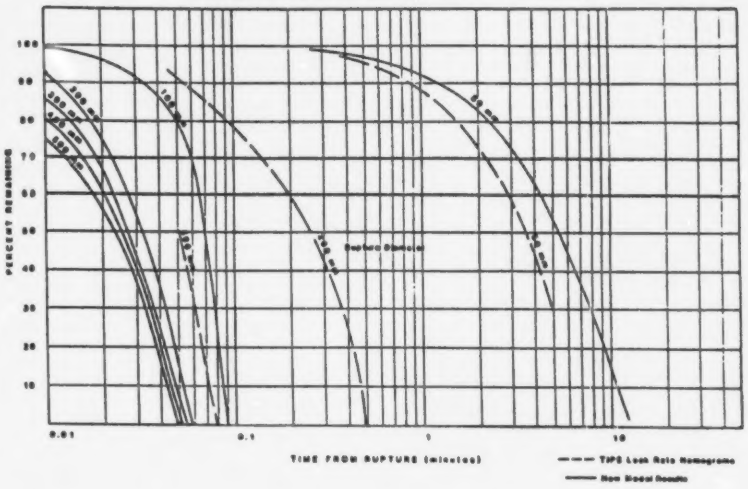
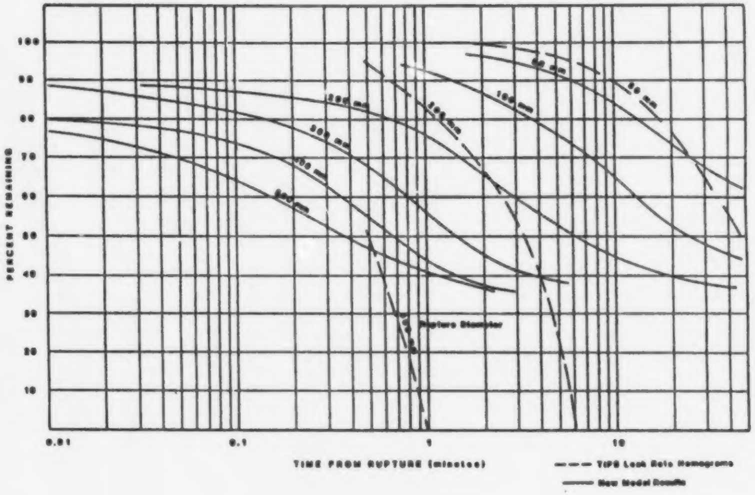


FIGURE 11

HYDROGEN SULPHIDE DISCHARGE NOMOGRAPH - HOLE IN TOP OF RAILWAY TANK CAR



HAZARD ANALYSIS OF PROPANE TANK CAR FAILURES IN A SPECIFIC LOCATION

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ABSTRACT

Prediction of the effects of failure of containment of propane rail tank cars is usually undertaken without reference to topographical considerations. The results of such analyses do not adequately present the possible impact of the results of the failure on districts with an escarpment adjacent to the site of the propane release.

In this paper, the potential consequences of propane releases from tank cars near to the base of a sloping hillside, are examined. The work includes an investigation of the effects of thermal radiation on the slope and an analysis of the blast effects in the area of the accident.

INTRODUCTION

Required as a fuel and as a petrochemical feedstock, liquefied petroleum gas (LPG, commercial propane) is routinely transported by rail tank cars to receivers remote from delivery pipelines. Transport legislation governing the design, construction, labelling and loading of propane tank cars provides regulations by which shipments are made as safely as possible (CTC, (1984)).

A number of recent tank car accidents resulting in the release of propane into the environment near populated regions (Eco/Log Week (1985 a), May (1984)) have focused public attention on the hazard potential of this material and the risks it poses (Burton and Post (1983), Geffen (1980)).

Examination of the accidents at Crescent City, Ill., Mississauga, Medonte Township and Toronto, Ontario, and Winnipeg, Manitoba (Lees (1980), May, (1984), Eco/Log Week (1985 a)) reveals the following:

a) Consequences arising from the failure of containment of tank cars laden with propane liquid and/or vapour can vary; and
b) Sharp contrasts exist between release site topographies.

The hazards associated with propane storage and shipping have been the subject of intense research and discussion in recent years. However, release consequence analyses postulating the effects of failure of containment of propane tank cars usually do not consider topographical influences. The results of such analyses do not adequately describe the possible resulting effects of the failure on districts with an escarpment adjacent to the site of the propane release.

The purpose of this paper is to examine the hazard potential of propane releases from rail tank cars near to the base of a sloping hillside. Consideration is given to ambient temperatures of -10°C and +20°C. Release consequences are postulated assuming the following:

a) Propane tank cars may be laden with liquid and/or vapour; and
b) A source of ignition may or may not be present.

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PROPANE SHIPPING CONSIDERATIONS

Aspects of Physical and Chemical Properties of Propane

The hazards presented by propane shipments stem from the following properties of the material, which form the bases for the release consequence analyses described in this paper:

a) The low boiling point of propane (-42°C) necessitates the transportation of large quantities of material in the liquefied state. Liquefaction is achieved by refrigeration or pressurisation. In this paper, only pressurised rail shipments are considered. Tank car vessels must be manufactured to withstand the stresses exerted by the vapour pressure of propane, which is a function of the ambient temperature. Pressurised liquefaction results in the material being retained in a state of superheat; the bulk material temperature is higher than the normal boiling point of the liquid. The degree of superheat is an important factor in determining the fraction of liquid flashed-off as vapour and the extent of the resulting vapour cloud following failure of containment.

b) Propane has a greater specific gravity than air and dispersion of released vapours will be controlled to a large degree by gravity.

c) Propane can form potentially flammable mixtures with air (2.2-9.5%) posing a fire (thermal radiation) and explosion hazard.

Rail Tank Car Design Criteria

Propane (LPG) is classified as a dangerous material in the federal "Transportation of Dangerous Goods Act" (Transport Canada (1985)) and must be shipped in tank cars designed, constructed, marked and loaded in accordance with the "Regulations for the Transportation of Dangerous Commodities by Rail" (CTC(1984)) established by the CTC.

Propane can only be carried in Class 105, 106, 111, 112 and 114 tank cars, each Class being subdivided by pressure ratings based upon the degree of pressurization required.

Regulations now require that all Class 112 and 114 tank cars transporting propane be fitted with the following safety features:

a) Thermal protection to prevent release of any of the vessel's contents (except through the safety valve) when the container is subjected to a pool fire for 100 minutes and/or a torch fire for 30 minutes;

b) Protective head shields capable of withstanding impact velocities up to 29 kph; and

c) Coupler vertical restraint system (Double Shelf Couplers) which resist disengagement under certain applied vertical loads.

In view of the increased use of Class 112 propane tank cars over recent years (Geffen (1980)) and the involvement of Class 112 and 114 propane tank cars in the Mississauga train derailment (Grange (1980)), the release consequence analysis that follows is concerned only with the insulated Class 112J340W propane tank car.

RELEASE SITE TOPOGRAPHY

Release consequence analyses undertaken to predict the effects of failure of containment of propane storage and shipping vessels routinely assumed "ideal" conditions, i.e. flat terrain without nearby obstructions. In particular, such simplifications are usually made with heavy gas dispersion calculations.

Topography of the release site not only influences the dispersion of heavy gases, but also directly affects the propagation of a flame front through a flammable vapour cloud mixture, the impact of thermal radiation and the trajectories of vessel fragments.

Seldom are "ideal" topographical conditions encountered along propane tank car shipping routes. The Canadian prairies approximate such perfect conditions, but examination of previous accidents reveals that a large proportion of propane releases occurred near busy population centres (Lees (1980), May (1984), Eco/Log Week (1985 a)).

The topographical features of the release site considered in this paper are based upon the characteristics found in an actual residential district through which a large number of propane tank cars routinely pass. In Figure 1, the release site geometry which has been simplified for the purposes of this study, is shown; two sets of tracks run parallel to and along the base of a 45° escarpment. The track runs straight on the west side of the pedestrian crossover bridge but begins a long sweeping bend northward to the east of this structure. Hydro-electric transmission towers on the south side also follow the track layout. The area bounded by the escarpment to the north and the tracks 40 m to the south is free of obstructions, while deciduous trees and shrubbery cover the entire escarpment. Housing to the south is as close as 8 m to the tracks. To the north, a school is situated atop the hill.

The propane release point chosen for this study is also shown in Figure 1. There are no track switches in this area and the track is of continuous welded construction. The train track dynamics dictated the feasibility of a possible derailment at the west end of the sweeping bend for traffic moving westbound.

HAZARD PHENOMENA ARISING FROM PROPANE TANK CAR FAILURES

The important parameters required to describe and estimate the hazard potential of propane are as follows:

a) Type and quantity of material involved
b) Duration of release
c) Point of discharge
d) Type of aperture
e) Fluid dynamics
f) Topographical and meteorological conditions
g) Source of ignition
h) Quantity of vapour in the flammable range
i) Explosion potential.

Typical tank car emission situations include complete rupture, fluid discharge through an aperture located above or below the liquid level and gas venting. The discharging vessel itself may be located below, at or above ground level. For the purposes of this study, it is assumed that complete vessel rupture occurs at ground level. Hence, the maximum possible quantity of vapour released spontaneously primarily depends upon the initial mass of pressurised superheated liquid retained in the tank car and the bulk material temperature prior to failure of containment.

Rail transport regulations prescribe the maximum permitted filling densities for propane tank cars for the summer (April-October) and winter (November - March) periods. In Table 1, the vapour/liquid masses and volumes of pressurised propane initially contained within liquid filled tank cars subject to ambient temperatures (T_A) of -10°C (winter) and 20°C (summer) are given.

TABLE 1: MASS OF PROPANE IN TANK CAR PRIOR TO RELEASE

	T_A = -10°C	T_A = 20°C
Maximum Permitted Filling Density (%)	48.39	46.50
Vapour Mass in Tank (kg)	157	326
Vapour Volume in Tank (m³)	21	18
Liquid Mass in Tank (kg)	60333	56674
Liquid Volume in Tank (m³)	110	113
Total Mass (kg)	60490	57000
Total Volume (m³)	131	

Propane discharged from tank cars into the environment will in time disperse if no source of ignition is present. However, the question of safe dispersion depends upon the conditions of release since propane behaves as an asphyxiant in high concentrations. Thus, it should be noted that safe dispersion does not necessarily occur when there is no source of ignition present.

If the released propane fires, the mode of combustion depends upon the nature of the flammable mixture at the point of ignition (size, shape, degree of confinement, composition), the nature of the ignition source (homogeneous, point source) and the ignition delay. The combustion process may be described in terms of whether the flames are (a) premixed or diffusion, and (b) stationary or propagating (Considine, et al. (1982)). The potential fire and explosion hazards presented by propane tank cars are summarised in Table 2.

TABLE 2: MAJOR FIRE AND EXPLOSION HAZARDS WITH PROPANE TANK CARS

Fires	Explosions	
Pool	Confined:	Combustion of Vapour
Jet	Unconfined:	Boiling Liquid Expanding Vapour Explosion (BLEVE)
Flash		Fireball
		Unconfined Vapour Cloud Explosion (UVCE)

The foregoing combustion processes may be initiated by the ignition sources enumerated in Table 3. The important criteria particular to each class of ignition source are also tabulated.

TABLE 3: SOURCES OF IGNITION

Homogeneous		Point Sources
Direct Heating Adiabatic Compression		Electrical Discharges 1) Power Circuits 2) Static Frictional Sparks
	Hot Surfaces Flames Hot Gas Jets	
	Criteria	
Temperature Geometry of Vessel		Minimum Ignition Energy
	Composition of the Vapour Phase	

Pool and jet fires may be considered to be stationary diffusion flames where ignition has taken place close to the source of release (Considine, et al. (1982) and Crawley (1982)). A pool of liquid flammable material must form following failure of containment for a pool fire to occur. Hence, pool fires are more likely to develop from releases of pressurised superheated fluids with low flash fractions. Jet flames can also form from pressurised releases.

Examples of propagating diffusion flames include fireballs and diffusion flash fires resulting from the delayed ignition of a poorly dispersed vapour cloud, the bulk of which is above the upper flammable limit. However, since the cloud's extremities are within the flammable range because of admixture with air, flame propagation through the peripheries rapidly envelops the fuel rich core in flame. Subsequent burning is relatively slower since the combustion process is controlled by the rate of entrainment of air and its mixing with fuel; combustion continues circumferentially. This phenomenon is commonly referred to as a fireball.

If the vapour cloud has a large diameter to height ratio, then diffusive burning at the point of ignition may be complete prior to flame propagation around the cloud periphery. Consequently, the cloud burns more like a flash fire with a thick band of flame making up the reaction zone.

Fireballs are more likely to occur following the ignition of an instantaneous release of pressurised flammable material. Diffusion flash fires arise from the ignition of slumped hemispherical clouds and plumes from liquid spills.

Propagating premixed flames may be slow burning with low overpressures being generated (flash fires) or burning with increasing frontal velocity creating large overpressures which may be transmitted beyond the vapour cloud's boundaries (UVCE).

For the purposes of this study, the following damage criteria listed in Tables 4 and 5 were adopted for thermal radiation effects and blast wave overpressures respectively (Clancey (1977 a), Considine,et al.(1982), Crawley (1982), Drysdale (1985), Lees (1980), Lihou, et al. (1982), Roberts (1982), Robertson (1976)).

TABLE 4: OBSERVED EFFECTS OF RADIANT HEAT FLUXES

Observed Effect	Radiant Heat Flux ($kW.m^{-2}$)	Duration(s)
Maximum for indefinite skin exposure	1	
Pain during skin exposure	10.4	3
	6.4	8
	4.7	10
Skin blistering[1]	20	4
	16	5
	6	20
1% lethality[2]	117	4
	35	20
Pilot ignition of wood	12.6	1000
Pilot ignition of cellulosic material[2]	66	4
	34	20
Spontaneous egnition of fibreboard	52	5
Process equipment damage	37.8	1000

1. Lihou, et al. (1982) notes the following correlation relating incident flux density ($\bar{q}_2$ in $kW.m^{-2}$) to duration (t_e in s) which will cause severe blistering:

$$\bar{q}_2 = 50/t_e^{0.71}$$

2. Linear interpolation on a log/log plot is permissible for intermediate durations (Roberts (1982)).

TABLE 5: BLAST DAMAGE CRITERIA

Peak Overpressure (kPa)	% Casualties	Damage
< 7	0	Window breakage, minor building structural damage.
7 - 20	10	Walls collapse
20 - 35	25	Reinforced structures distort, wooden utility poles snapped
30 - 50	70	Nearly complete destruction of houses, loaded wagons overturn
> 50	95	Total destruction of buildings, extensive damage.

RELEASE CONSEQUENCE ANALYSES

Quantity of Vapour Released from Liquid-Filled Tank Cars

Upon complete vessel rupture, the pressure drops almost instantaneously and a significant proportion of the liquid flashes to vapour. Liquid droplets may be thrown into the air; their size depends upon the degree of superheat. At low superheats, large droplets may be ejected and fall back either into the vessel or onto the ground. Higher degrees of superheat result in smaller droplets forming into an evaporating aerosol.

The quantity of material released by instantaneous depressurisation can be determined from thermodynamic correlations. The amount of vapour emitted by complete rupture may be obtained by equating the changes in latent heat of vapourisation to the sensible heat in the liquid. Vapour release estimates calculated for complete vessel rupture and adjusted for spray entrainment are summarised in Table 6.

TABLE 6: VAPOUR RELEASE ESTIMATES FOR COMPLETE RUPTURE

	T_A = -10°C	T_A = 20°C
Mass of vapour flashed off (kg)	21877 (36%)	42264 (74%)
Mass of liquid remaining (kg)	38613 (64%)	14736 (26%)
TOTALS (kg)	60490 (100%)	57000 (100%)

The remaining liquid will continue to vapourise, albeit slowly because of heat and mass transfer limitation, but this is of no significance in flammable gas cloud formation.

Vapour Cloud Sizing

The dispersion of propane is influenced by the fact that the gas is heavier than air and the release site is at ground level.

At ambient temperature, propane (molecular weight = 44.11)is heavier than air (molecular weight = 29). During vapour flash-off arising from tank car rupture, the temperature of the expanding gas approaches the normal boiling point of the liquid as the sensible heat of the liquid is transferred to latent heat of vapourisation. Liquid droplets sprayed out of the tank car, cool the spreading cloud as they evaporate.

The dispersion of propane vapour cannot be treated in the same manner as the dispersion of gases with neutral buoyancies (densities approximately equal to air), the latter being influenced by turbulence in the atmospheric boundary layer. Van Ulden (1974) noted that the Gaussian dispersion models used for neutral gases and not corrected for density spread overestimated vertical spreading and underestimated horizontal spreading of heavy gases. Furthermore, Gaussian models do not account for an initial decrease and then increase in the height of the cloud. Van Ulden (1974) reported that density spread against the wind is likely to occur during the initial decrease in height.

The release of propane vapour at ground level may alter the fluid flow pattern in the atmosphere near the release site. Subsequent motion of heavy gas and mixing with air involves complex interaction with the atmospheric flow field and the flow of gas which may be influenced by gravitational forces.

For large releases, the gravity induced flow and resulting interaction with the atmospheric flow can determine the shape and extent of the area which is exposed to flammable or asphyxiating gas concentrations. The early phases of cloud formation, motion and dispersion following release of large quantities of gas involve density-stratified flows which are not well understood (Havens (1982)).

For the purposes of this paper, rapid, hand-calculated estimates of propane vapour cloud sizes were obtained using the dispersion models for instantaneous releases reported by Clancy (1977a). The results are summarised in Table 6. Neutral atmospheric conditions with no wind were assumed.

TABLE 6: PROPANE VAPOUR CLOUD SIZE

	T_A = -10°C	T_A = 20°C
σm (m)	25.33	31.54
r_l (m)	44	55
r_u (m)	0	0
Flammable quantity (kg)	14585	28176
Downwind position (m)	550	705
Inert downwind position (m)	1000	1253

where: σm = standard deviation when cloud is at maximum potential
r_l = radial distance to lower flammable limit
r_u = radial distance to upper flammable limit.

The results demonstrate the massive extent of the vapour clouds. Under ideal topographical conditions, the discharged vapour would initially form into a hemispherical cloud and become more pancake shaped as dispersion causes the diameter to increase.

However, considering the release site topography in Figure 1, the movement of propane vapours to the north would be blocked by the escarpment 40 m away. It is important to note that the mixture would be flammable up to the base of the hill.

Dispersion to the south would be hindered by the obstacles present (houses and trees). The vapours would flow around these "blocks", seeping into the basements of some houses and collecting in any depressions. The point concentrations of the cloud would be routinely changing from place to place as the material dispersed through the residential area. Pockets of flammable mixtures would collect in several areas, possibly remaining there for a long time. Cloud movement to the south would be slow and restricted but not stopped. This is important to note when considering the time it would take for the area to be cleared of any vapour after the release.

Dispersion would in general parallel the escarpment. Cloud movement would follow the railway corridor to the east and to the west. The cloud would become cigar-shaped as it moved along the paths of least resistance. At the base of the hill, the mixture would remain flammable for a long period as the cloud elongates and disperses at the edges to the east and west as well as to the south, although to a lesser degree. The cloud centre will not displace to any great extent. Dispersion of the vapours would take a long time and would be greatly assisted by an east-west wind.

Pool Fires

Pool fires present thermal radiation hazards with the potential for direct flame impingement on adjacent objects. Incidence radiant heat fluxes are influenced by flame geometry (size and shape of the flame envelope), source strength (temperature and thermal emissive power of the flame gases), view factor and separation distance between source and target and atmospheric attenuation of thermal radiation.

Flame geometry depends upon the pool diameter and weather conditions. Increased wind speed tilts the flame envelope, thereby increasing radiant heat fluxes on downwind targets, since separation distances are lessened. Furthermore, there is an increased likelihood of direct flame impingement on these objects.

Source strength coupled with view factor, separation distance and atmospheric attenuation of thermal radiation prescribe rate of heat transfer to objects.

Because of limitations inherent in the point sources modelling technique (incident heat fluxes cannot be calculated on receivers closer than five pool diameters to the source), the solid flame technique was adopted for prediction of radiant heat transfer.

A review of the release estimates in Table 6 indicates that a propane pool fire is more likely to happen following a tank car rupture in winter.

Using the following experimental results obtained by Mizner, et al. (1982) for LPG pool fires in a 20 m diameter pre-cooled circular bund:

a) Average surface thermal emissive flux = 48 $kW.m^{-2}$

b) Flame length = 47 m

c) Mass burning rate = 0.13 $kg.m^{-2}.s^{-1}$.

Calculated radiant heat fluxes incident on targets adjacent to the release site are summarised in Table 7 and shown in Figure 2. The tabulated results assume zero wind conditions over a 20 m diameter pool fire which is burning for 16 minutes.

TABLE 7: VARIATION OF INCIDENT THERMAL RADIATION WITH RADIAL DISTANCE FROM PROPANE POOL FIRE

Incident Flux[1] ($kW.m^{-2}$)	Distance Along Ground[2] (m)
Greater than 12.6	Less than 15
10.4	21
6.4	32
5	Base of escarpment
2	Top of escarpment
1	116

1. Refer to Table 4 for significance of chosen values.
2. From flame centre-line to target.

Shielding afforded by housing, vegetation (different for winter and summer) and vehicles influence the actual incident fluxes within each bounded area and hence the exposure time, the number of both injuries and fatalities and the amount of property damage. However, secondary fires will most likely erupt from cellulosic-bearing shields less than 15 m from the pool fire.

Faced with the real situation, panic-stricken people will not think to shield themselves, but will try to move away from the fire as quickly as possible. Radiant heat fluxes will strike their largely unexposed (clothed) backs. Under these circumstances, exposure times will increase, but effective thermal fluxes will decrease with radial distance from the fire.

BLEVE/Fireball

BLEVE is the acronym for a Boiling Liquid Expanding Vapour Explosion. This phenomenon can occur when a propane tank car is subjected to the intense heat of an external fire, which induces vessel failure and effects the release of its contents.

As the liquid-filled tank car is heated, the vapour pressure inside the container begins to rise reaching the set-to-discharge pressure of the relief valve. Liquid in contact with the walls of the vessel acts as a heat sink and conducts the heat away from the metal. For a tank with a relief valve with a set-to-discharge pressure of 1.7 MPa, the temperature of the liquid will not exceed 50°-60°C. The tank metal is able to absorb the pressure stresses exerted in this temperature range. However, the container structure will be stressed in tension. As the vapourisation process continues, the quantity of liquid in the vessel decreases, thereby exposing more metal to the vapour phase. Since the vapour is relatively non-heat conductive and has little heat absorbing capacity, the container will fail, causing the release of the remaining contents, since the tank metal can no longer withstand the stresses imposed by the surrounding temperatures.

Liquid vapourisation is accompanied by a large liquid-to-vapour expansion which can provide the energy for propagation of cracks in the tank structure, propulsion of vessel fragments and rapid mixing of vapour in air which is quickly ignited by the surrounding fire, producing aerial fireballs. Up to 28% of the vessel contents can be sufficiently well-mixed with air to undergo percussive deflagration (Lihou, et al. (1982)). Crawley(1982) notes that the release of this energy can produce blast overpressures up to 0.05 MPa at the source.

The violence of the flash vapourisation process causes the ejection of a significant quantity of aerosol droplets. Although, many of the droplets burn, a small number remain unburned as they are propelled rapidly away from the fire. McKinnon (1976) reported that dissolved spots in asphalt paving caused by liquid droplets were observed up to 0.8 km from the site of an LP-Gas BLEVE.

However, the majority of droplets become entrained in the ignited flammable vapour cloud. Hence, there is an increased tendency for soot formation in the fireball (Lihou, et al. (1982)).

Using the heat and mass balance correlations and view factors between fireballs and targets developed by Lihou, et al. (1982), radiant heat fluxes calculated for a propane tank BLEVE in winter are listed in Table 8 and shown in Figure 3.

TABLE 8: INCIDENT HEAT FLUXES FROM PROPANE TANK CAR BLEVE IN WINTER

	(T_A = 20°)
Mass of propane = 60490 kg	(57000kg)
Fireball diameter = 136 m	(133 m)
Combustion duration = 12 s	(12 s)
Combustion temperature = 1809K	(1809K)
Emitted flux density = 607 kW.m^{-2}	(607 kW.m^{-2})

INCIDENT FLUX DENSITY[1] (kW.m^{-2})	HAZARD RANGE[2] (m)
139	Top of escarpment
133	Top of escarpment
45	140
41	145
28	175
8.5	270 (267[3])

1. The values chosen were interpolated from the criteria listed in Table 4 for combustion duration of 12 s.
2. Distance radially along the ground from the centre-line of fireball to target.
3. Value calculated from: Rh = 3.29 $(m)^{0.4}$ (Lihou, et al. (1982)).

TABLE 9: FIREBALLS FROM PROPANE TANK CARS

	T_A = -10°C	T_A = 20°C
Mass of cloud (kg)	21877	57000
Initial diameter (Do)(m)	27	39
Final diameter (Dc) (m)	161	222
Final elevation (He)(m)	130	170
Combustion duration (s)	13	17
Combustion temperature (K)	2077	2085
Emitted flux density (kW.m^{-2})	1055	1072

TABLE 10: INCIDENT HEAT FLUXES FROM FIREBALL FROM PROPANE TANK CAR

Incident Flux Density[1] (kW.m^{-2})	Hazard Range[1] (m)
136	Top of escarpment
103	Base of escarpment
45	183
41	203
28	279
8	308 (278[2])

1. Refer to Notes 1 and 2 attached to Table 4.
2. Value calculated from: Rh = 5.10 $(m)^{0.4}$ (Lihou,et al. (1982)

The results summarised in Tables 8 and 9 were calculated from expressions adopted to predict the hazards presented by propane fireballs. The impact of the results is illustrated in Figure 4.

Flash Fire/Vapour Cloud Explosion

The analytical treatment of flash fires is not well developed. However, the effective thermal radiation intensity and duration of a flash fire arising from the ignition of a propane vapour cloud in winter (see Table 6) were calculated using the correlations presented by Lees (1980). The results are presented in Table 11.

TABLE 11: FLASH FIRE

Mass of vapour in cloud (kg) = 21877
Volume of cloud (m^3) = 2.9×10^9
Surface area of cloud (m^2) = 7.8×10^6
Effective thermal radiation intensity ($kW.m^{-2}$) = 1323
Effective duration of flash fire (s) = 0.04

Turbulence induced by the flame front propagating around obstacles within the cloud may cause a vapour cloud explosion (Wiekema (1984)). Using the correlations prescribed by Wiekema (1980) for predicting overpressures generated by vapour cloud explosions, it was estimated that the reflected shock overpressures at the top and bottom of the escarpment would be 20 kPa.g and 30 kPA.g respectively.

Confined Explosion

In the past, "empty" tank cars have been pressured to 0.5 MPa with natural gas to prevent any ingress of air and the formation of flammable mixtures. The explosion of one such "empty" tank car at the MacMillan marshalling yard in Toronto, Ontario, indicates the hazardous consequences of this practice (Eco/Log Week 1985a).

Amendments to the Canadian Transport Regulations now limit natural gas backfilling to 0.2 MPa. However, the potential for the formation of flammable mixtures remains, and ignition of the contents will result in a confined deflagration.

Table 12 indicates the variation of blast wave overpressures with radial distance from the confined explosion of propane tank car following the ignition of a stoichiometric ratio of propane in air at atmospheric pressure. Overpressures from the blast wave reflected from the escarpment are also tabulated.

TABLE 12: BLAST WAVE OVERPRESSURES

Maximum explosion pressure (T_A = -10°C) = 880 kPa
Initial shock pressure when vessel bursts = 365 kPag

Radial Distance from Vessel	Incident Shock Overpressure (kPag)	Reflected Shock Overpressure (kPag)
8	134	
10	98	
20	34	
30	19	
40	14	30 (base of escarpment)
50	12	
55	11	
60	11	
70	11	
80	10	20 (top of escarpment)

Vessel Fragmentation and Missile Damage

Although most studies of explosions concentrate on the overpressure effects produced by the ensuing blast wave, significant damage may be caused by the impact of flying primary and secondary fragments and objects.

Concentrating only on primary fragments ejected from the bursting vessel, the self-propelled fragment is assumed to be one-half of the tank cylinder which has severed perpendicularly to its longitudinal axis. The rocketing portion is free to move away from the rest of the constrained vehicle. The tank car head is considered as the jet-propelled fragment. Predicted tank car fragmentation velocities and hazard range calculated from the correlations given by Held, et al. (1982) for the confined explosion described earlier are summarised in Table 13.

These values of range are quite distinct from those obtained for tank cars filled with propane. On failure, sections of tank can rocket and be propelled up to distances of the order of 700 m.

TABLE 13: FRAGMENTATION HAZARDS

	T_A = -10°C	T_A = 20°C
Maximum explosion pressure (MPa)	0.88	0.79
Self-Propelled Tank Car		
Mass of rocketing vessel (kg)	12858	12858
Maximum vessel velocity ($m.s^{-1}$)	14.5	13
Maximum range (assuming no air drag) (m)	21	17
Jet-Propelled Tank Head		
Mass of head (kg)	983	983
Fragment peak velocity (ms^{-1})	27.5	27
Maximum range (m)	77	74

CONCLUSIONS

The transportation of dangerous commodities by rail has come under increased public scrutiny in recent years in the wake of a number of rail accidents. The hazards presented by dangerous goods shipped along current and future railway routes must be evaluated. This paper has shown that while it is often easier to idealise the topographical features surrounding a release site when postulating the release consequences, accuracies of results obtained from analytical models incorporating real conditions can be increased significantly. The methodology used is not limited to assessing the hazard potential of propane tank cars but can be applied to other postulated release consequence analyses.

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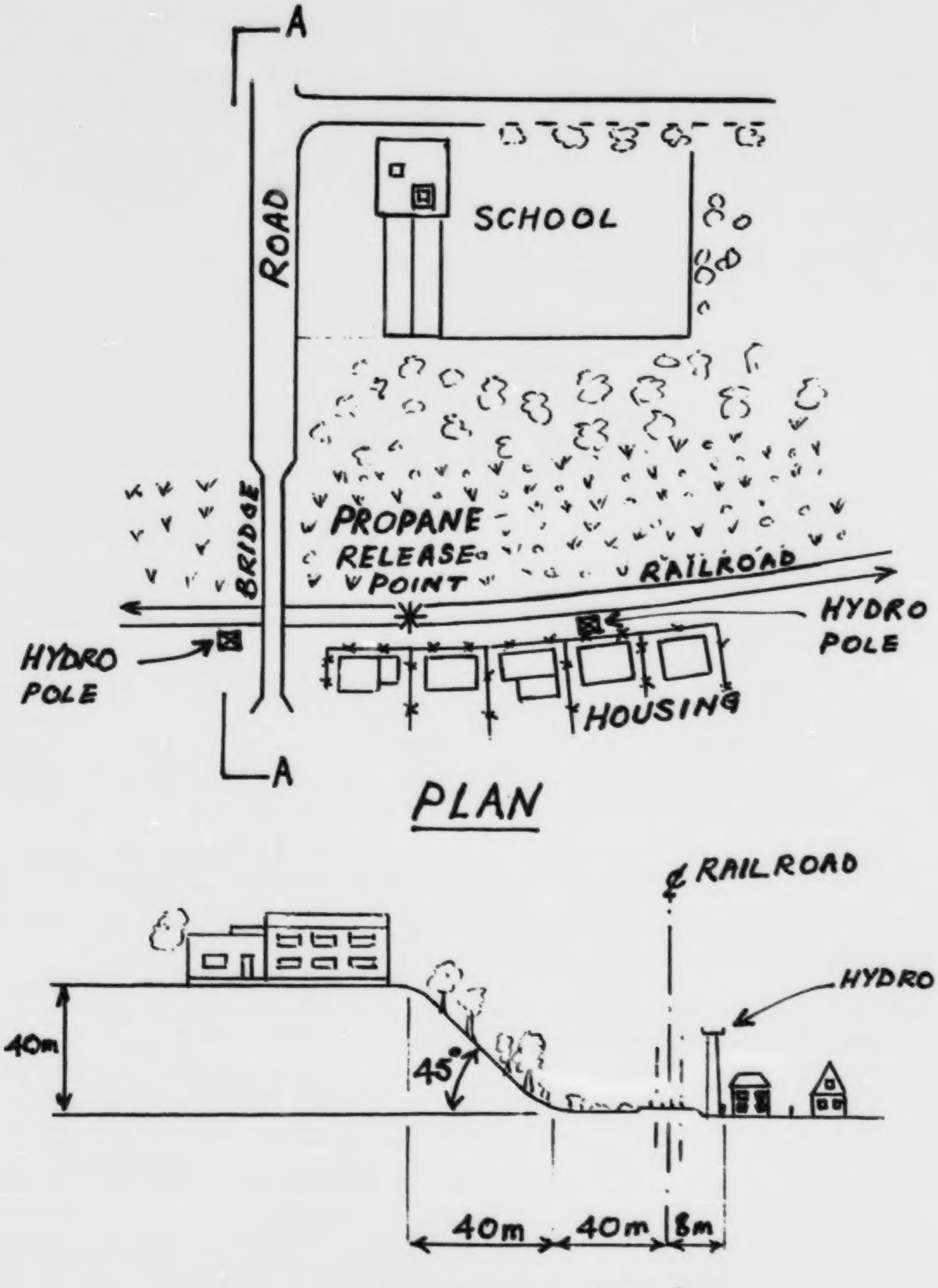
A
ROAD
SCHOOL
BRIDGE
PROPANE
RELEASE
POINT
RAILROAD
HYDRO
POLE
HYDRO
POLE
HOUSING
A
PLAN
RAILROAD
HYDRO POLE
40m
45°
40m
40m
8m

SECTION 'A-A'

FIGURE 1

RELEASE SITE - TOPOGRAPHY

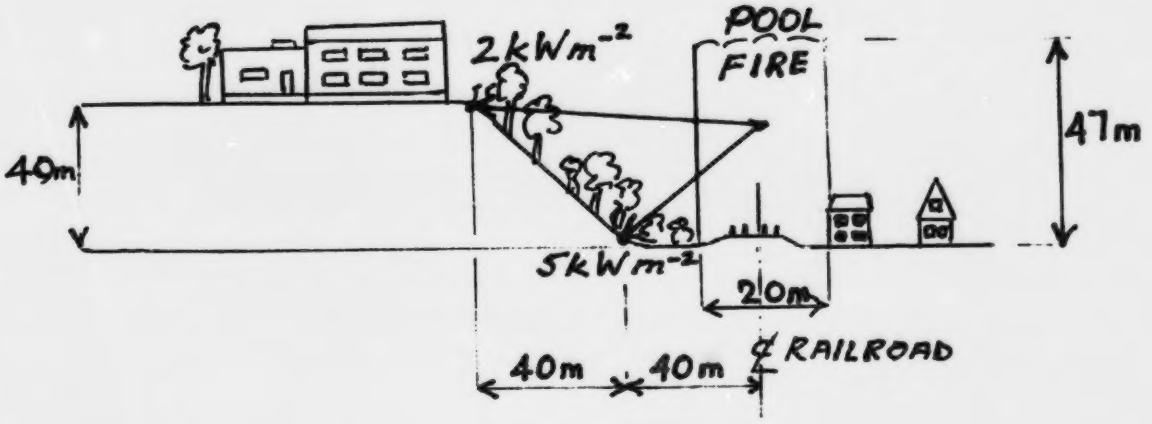
POOL
FIRE
2kWm^{-2}
47m
49m
5kWm^{-2}
20m
℄ RAILROAD
40m
40m

FIGURE 2

INCIDENT HEAT FLUXES FROM POOL FIRE

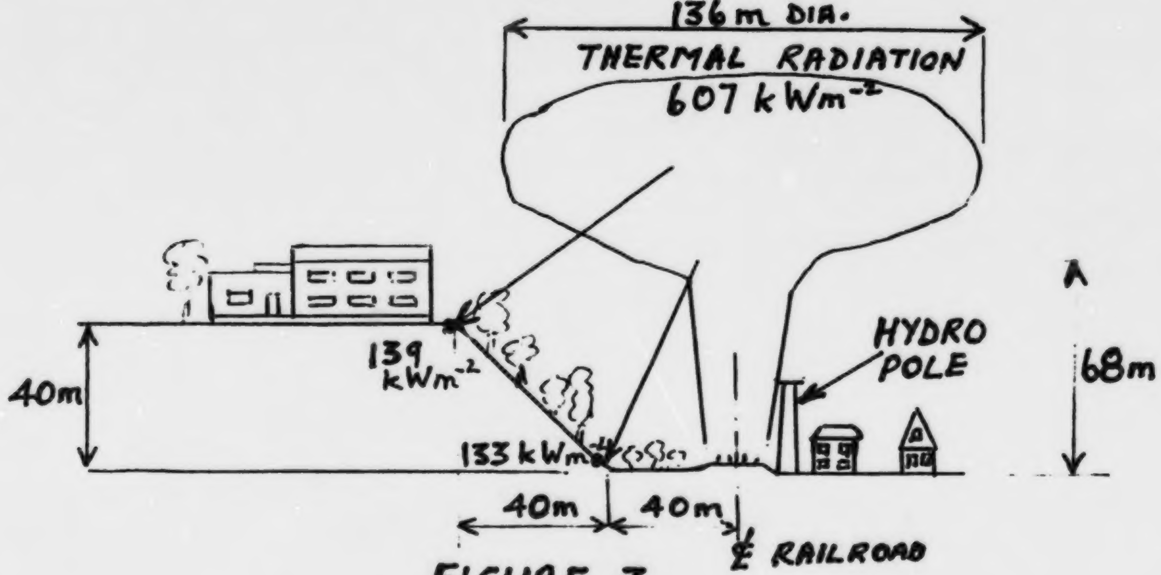
136m DIA.
THERMAL RADIATION
607 kWm-2
139 kWm-2
133 kWm-2
40m
HYDRO POLE
68m
40m
40m
℄ RAILROAD

FIGURE 3

INCIDENT HEAT FLUXES FROM BLEVE

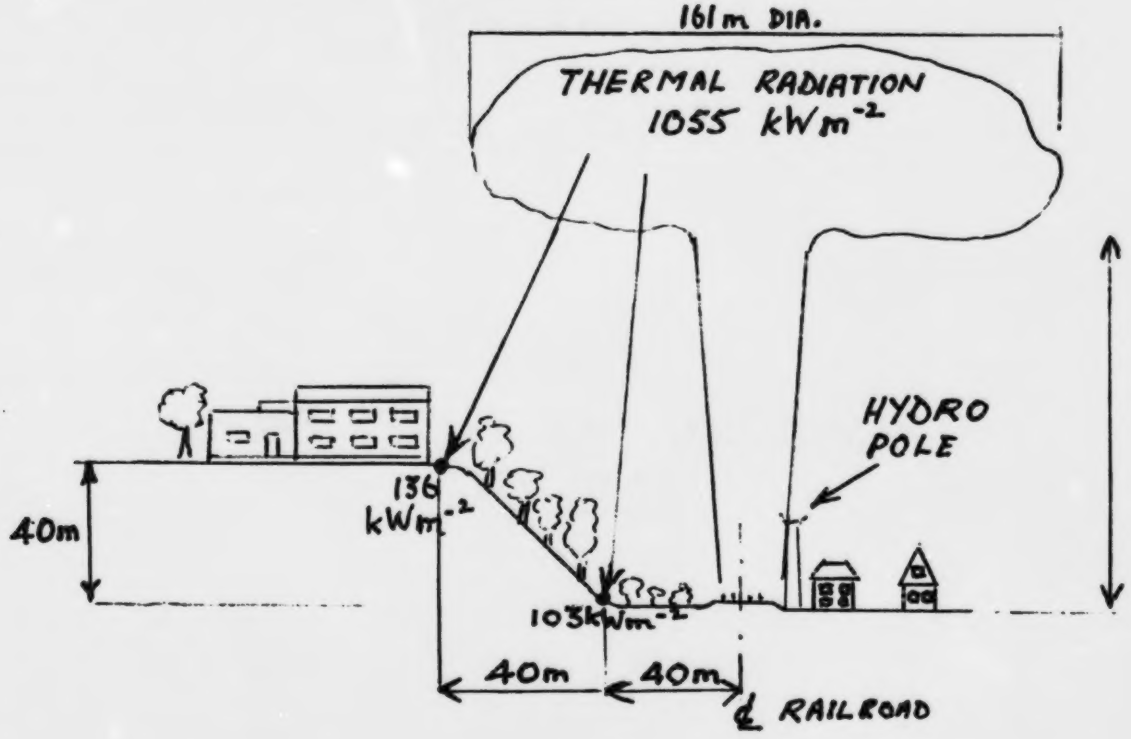
161m DIA.
THERMAL RADIATION
1055 kWm-2
136 kWm-2
103 kWm-2
40m
HYDRO POLE
40m
40m
℄ RAILROAD

FIGURE 4

INCIDENT HEAT FLUXES FROM FIREBALL

Spreading of Chemicals on Ice and Snow

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INTRODUCTION

When planning for or responding to chemical spills, it is useful to know, in advance, the likely spreading characteristics of the chemical. In particular it is helpful if the final spill area can be estimated and the time necessary to reach that area predicted. Any unusual spill characteristics should also be known in advance, for example, any tendency to be absorbed or evaporated or react. The spill area is a critical variable in the assessment of evaporation rate, which in turn controls atmospheric concentrations experienced by personnel.

This study concerns the behaviour of chemicals spilled on ice and snow, a common ground surface in much of Canada for much of the year. The general aims of the study are:

(i) to document by experiment, the general phenomena which occur when various chemicals are spilled on ice and snow;

(ii) to provide methods of estimating the final spill area as a function of volume spilled. (We only consider "instantaneous" spills in which a finite volume of chemicals is released rapidly.);

(iii) to estimate the time of spreading;

(iv) to develop a model of spill behaviour which can be linked to other models, for example, atmospheric dispersion and soil penetration.

In the case of snow and ice, a critical variable is the extent to which the chemical interacts with or dissolves ice, thus modifying the surface on which it is spilled. For example, low molecular weight alcohols will readily dissolve snow and ice and they may tend to create depressions in the ice surface and even "eat through" the ice to underlying water. A strong acid may release sufficient heat on contact with ice to melt an appreciable quantity.

There have been many studies of oil spreading on water, a few on land, but little study on snow and ice. Raisbeck and Mohtadi (1974) developed a model for crude oil spreading from a continuous leak on permeable and impermeable surfaces. Hoult et al. (1975) employed a statistical approach for determining the extent of an oil spill over Arctic ice. Chen et al. (1974) and Chen and Charles (1976) studied the rate of spreading of crude oil on an ice surface for the two of the three spreading stages known to exist. In each of these stages, one spreading force is balanced by one retarding force. The three stages are: gravity-inertia; gravity-viscous; and surface tension-viscous. Chen's studies addressed and correlated the rate of spreading in dimensionless form for the latter two spreading regimes.

MATHEMATICAL MODELS

The spreading behaviour of a chemical on snow, ice or absorbing terrain is a very complex phenomena. Thus, several models will likely be devised, each with a desired level of accuracy. Most complex are the numerical models in which the equations of motion are set up and solved in a multidimensional matrix. An example is the Farquar-McBean model (1984) describing spreading on and penetration into, soil. This model gives an accurate representation of reality, but it is difficult to use. The dimensionless number models of Chen described earlier are much simpler, but they do not treat absorption or evaporation, nor can they be easily modified to do so.

We believe that progress is best made in this subject area by postulating models, subjecting them to peer review and criticism in the expectation that the better and more useful models survive and are modified by other investigators. Accordingly, in this study we treat our data to two modelling approaches, the Chen dimensionless number approach and a novel "general" model which includes absorption, evaporation and snow and ice dissolution.

The Chen model essentially involves plotting log (area) or log (radius) versus log (time) in the expectation that linear regions will be obtained. Specifically, plotting log (area) versus log (time) should give a line of slope 0.4 in the gravity-viscous regime and (1-b)/2 in the surface tension-viscous regime, where b is a constant.

In the general model, a basic area-time relationship is proposed of the form

$$A = A_F\ (1 - \exp(-(t/\tau)^x))$$

where A is area, A_F is the final area at infinite time (t) and τ and x are constants. Regardless of the value of x, the area is 63% of the final area when t equals τ. τ is thus a "spreading time constant". Increasing x slows down the initial spreading and accelerates the later spreading. It controls the slope of the A-t graph when t equals τ, a large value of x giving a large slope.

The final area A_F is estimated from the initial spill volume (V), the volume change (until spreading stops) due to evaporation, absorption, etc. (ΔV), and a final equilibrium spill depth on the surface (h_F), such that

$$V - \Delta V = A_F h_F$$

Now ΔV is estimated as the algebraic sum of three terms

Loss due to evaporation $= h_E A_F$

Loss due to absorption in soil $= h_A A_F$

Gain due to dissolution of snow $= h_s A_F$

i.e. $\Delta V = A_F (h_E + h_A - h_S)$

In all cases the h terms represent mean values which apply at the time of cessation of spreading. For evaporation, we postulate

$$h_E = C_E K_E (Pv/RT)\tau$$

where C_E is a dimensionless constant, K_E is a mass transfer coefficient, (Pv/RT) is the dimensionless ratio of chemical concentration in air to concentration in the chemical phase (in which P is vapour pressure, v is molar volume, R is the gas constant and T is absolute temperature). The time term is τ and C_E thus "corrects" for the change in area with time.

Similarly for absorption we postulate,

$$h_A = C_A K_A \tau$$

where K_A is an absoption velocity controlled by the soil porosity.

For snow dissolution we postulate

$$h_S = \phi H_S$$

where ϕ is the volume fraction of water in the snow and H_S is the mean snow depth dissolved.

It follows that

$$A_F = V/(h_F + h_E + h_A - h_S)$$

The final equation is thus

$$A = \frac{V\ (1 - \exp(-(t/\tau)^x))}{h_F + \left[C_E K_E\ (Pv/RT) + C_A K_A\right]\tau - \phi H_s}$$

The advantage of this equation is that it is simple and contains terms for absorption, evaporation, and snow or ice dissolution. The constants which must be determined by experiment are as follows:

τ - spreading time constant which is expected to be primarily a function of viscosity

x - slope term

C_E - evaporation constant (probably close to unity)

C_A - absorption constant (probably close to unity)

h_F - final spill thickness which is expected to depend on surface roughness, viscosity and interfacial tension.

The terms K_E, P, v, T, K_A, ϕ, and H_S can be estimated directly from spill conditions and chemical properties, and are not adjustable.

EXPERIMENTAL

The experimental work can be divided into three sections:

(i) solubility of ice in various chemicals;
(ii) spreading of chemicals on ice;
(iii) spreading of chemicals on snow.

(i) Solubility Studies

This study is being undertaken to determine the extent to which the chemical dissolves snow and ice. This property can be estimated by determining the solubility of ice/water in the chemical, which is the maximum amount of snow/ice that dissolves in the chemical at a specific temperature. The solubility of water in various chemicals is reported in the literature (Polak and Lu (1973), American Petroleum Institute (1970)) but the list is small in comparison with the chemical in water solubility data. For chemicals of interest, in which the water in chemical solubility data were not available or did not apply to the current study, simple measurements of this solubility were conducted.

The study involved contacting an ice cube with a known volume (6-12 mL) of chemical in a sealed container for a period of 24 hours. The solubility of ice in the chemical was determined from the mass difference in the ice cube before and after the 24 hour period. These experiments were carried out at temperatures ranging from -5 to -20°C in a temperature controlled cold-room. From the experimental data and literature values, we can classify these chemicals into one of three categories:

1. Insoluble (Snow and Ice will not dissolve)

   This group consists of chemicals which have a small or negligible solubility of water in the chemical. An arbitrary value of less than 5% solubility by weight was chosen as the criteria for categorization in this group. Examples of chemicals in this category include: toluene, xylenes, alkanes, chloroform, benzene, gasoline, kerosene, dichloromethane, methyl isobutyl ketone, methyl methacrylate, ethyl acetate and aniline.

2. Partially soluble (Snow and Ice will partially dissolve)

   This group consists of chemicals which have a greater than 5% solubility but are not completely soluble. These chemicals, under certain conditions, may melt but not completely dissolve the ice. This results in the formation of two-liquid phases, consisting of a water-rich phase with a certain amount of dissolved chemical and a chemical-rich phase with some dissolved water.

   Examples of chemicals under this classification include: butanol, pentanol, and methyl ethyl ketone.

3. Completely soluble

   Chemicals in this group are soluble in all proportions at typical winter temperatures. These chemicals will dissolve snow/ice until:

(i) There is no more snow or ice; or

(ii) The concentration of water in the chemical reaches a point such that the surrounding temperature equals the freezing point of the water-chemical mixture. At this point the mixture may freeze. However, in some cases, the heat liberated from the dissolution process may delay the onset of freezing.

Chemicals under this category include glycerol, ethylene glycol, methanol and sulfuric acid.

We are attempting to classify most of the liquid chemicals in the Environment Canada's list of priority hazardous materials.

(ii) Spreading on Ice

Initial spreading experiments involved spilling various aqueous solutions on a smooth glass surface. The advantage of using aqueous solutions of chemicals such as glycerol and ethylene glycol, besides being relatively non-hazardous, is that desired properties such as viscosity and surface tension can be easily selected. These experiments were followed by spreading experiments on artificially prepared smooth ice surfaces. The selected chemicals for the ice experiments were mineral oil, n-pentanol, m-xylene and a petroleum-based product called Bayol 35. These chemicals were selected on the basis of low solubilities of ice, low evaporation rate, a relatively non-hazaradous nature and their wide range of viscosities (0.9 - 1500 cp).

All spreading experiments involved spilling 25- 75 mL of chemical (with dye added for increased visibility) from a glass tube with a rubber ring attached to one end. The rubber end of the glass tube was placed firmly against the solid ice/glass surface and a known volume of chemical was poured into the tube. Time was recorded with a stopwatch which was started when the tube, containing the chemical, was lifted. The spreading rate as well as the stopwatch reading were recorded with a video camera.

We are currently attempting to correlate the final area for the glass and ice experiments and the spreading rate for the ice experiments with parameters such as spill volume, viscosity, and the wetting characteristics of the solid surface. Experiments on rough ice surfaces are also being undertaken.

(iii) Spreading on Snow

For chemical spills on a snow surface, the volume spilled is often large such that the chemical penetrates downward with little radial spreading until it reaches the underlying ground or ice surface. At this point, the chemical may spread radially along the solid surface.

We will attempt by experiment to determine and correlate the extent and rate of this radial speading in the snow medium. We also plan to study and determine the extent of dissolution of snow for chemicals which have a high water solubility.

CONCLUSIONS

A tentative chemical spreading model has been developed to estimate the final spill area of chemical spills as well as the spreading rate and the time of spreading. The advantage of this model is that it is simple and includes the effects of evaporation, absorption, and snow/ice dissolution. Experiments are currently being conducted on snow and ice surfaces to determine some of the constants and the parameters for this model.

Furthermore, the general phenomena which occur when chemicals are spilled on ice and snow are being studied. In particular, a classification system has been proposed to categorize chemicals according to the extent to which it dissolves ice and snow. An attempt is being made to classify most of the liquid chemicals in the Environment Canada's list of priority hazardous materials.

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Titre : Deux systèmes informatisés pour la prévision du comportement des pollutions en milieu marin.

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Résumé : La présente communication décrit deux systèmes informatisés pour la prévision du comportement des pollutions en mer.

Pour le premier, il s'agit d'un système de programmes, accessible aux non-informaticiens, destiné à prédire l'évolution d'une pollution par hydrocarbures. Pour le réaliser, on a couplé interactivement trois modèles prédisant, d'abord, l'évolution des hydrocarbures en surface, ensuite, l'advection-diffusion de la phase dispersée, enfin, l'impact immédiat sur les ressources vivantes de la mer. Ce système est opérationnel depuis octobre 1985.

Le deuxième système est actuellement en cours de réalisation. Il devra décrire l'évolution des substances chimiques susceptibles de s'évaporer. Pour ce faire,on couplera deux modèles principaux : l'un pour prévoir le comportement de la nappe de polluant à la surface de la mer, l'autre pour prévoir l'évolution du nuage gazeux. Ces modèles seront couplés interactivement et l'impact d'un éventuel nuage toxique sera aussi envisagé.

SOURCE TERMS FOR DISPERSION MODELLING OF RELEASES OF HEAVY GASES

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INTRODUCTION

This research has been concerned with the quantification of source terms for dispersions of gases transported as liquids under pressure, e.g. liquefied petroleum gases (LPG), ammonia and chlorine. In a collision, failure of containment may result that allows releases which vary in rate of discharge according to the major parameters of the system.

In this paper, consideration has been given to liquefied gas transport by railcars; these considerations are also applicable to tank trucks. Similar model development has also been completed for liquefied gases carried by ocean-going carriers and truck tankers.

Impacts of vehicles occur over a wide range of relative velocities and the masses involved differ with the particular accident scenario. Hence the magnitude of the breach in containment will be defined and the consequent magnitude and conditions of flow will exhibit temporal variation. In order to improve the estimate of downwind concentrations of the released fluid, definition of the source term based on these considerations is required.

In order to show the methodology, a coupler impact on a tank car head has been reported here. It is this accident scenario that accounts for approximately two-thirds of punctures in railcars.

The first requirement for definition of the source term was to model the size of the hole. This required synthesis of various impact and fracture studies published in the literature. Secondly, using general principles of engineering, a model for predicting the release rate from the hole was developed.

CONTAINMENT SYSTEM FAILURE

For railcars and tank trucks transporting liquefied gases, the most frequent cause of cargo loss occurs from mechanical damage in the form of punctures or fractures (AAR, 1972; Transport Canada, 1980). In collisions or derailments, significant crack propagation leading to rupture will not occur, unless the ambient temperature is low and the metal is below the ductile to brittle transition temperature where brittle fracture propagation can occur.

The parameters which determine whether breach of containment occurs and if so, the size of the breach are:

(i) size and shape of impacting object
(ii) kinetic energy
(iii) impact angle
(iv) internal tank pressure
(v) ambient temperature, and
(vi) condition of the tank (i.e. any previous flaws)

When the striking object is blunt, the tank fails from stretching. If the striking object is sharp, the metal will shear. The size of the hole depends on the depth of penetration and shape of the impacting object.

Coupler Impact Scenario

The impact scenario may be simplified to the consideration of the collision of 2 masses the magnitude of which will vary according to the composition and state of the train.

For derailments, Peters et al. (1980) established that the number of cars that significantly affect a tank car are at most the three following cars travelling at an average velocity V_1, and the two preceding travelling at an average velocity, V_2. If the mass of the three striking cars is M_1 and the three struck cars M_2, then

$$KE_i = KE_f + E_c$$

where KE_i = initial kinetic energy = $\frac{1}{2} M_1 (V_1 - V_2)^2$,

KE_f = final kinetic energy = $\frac{M_1}{M_1+M_2} KE_i$ (Peters et al., 1980)

E_c = absorbed collisional energy and is equal to $E_d + E_i$, where E_d is dissipated energy in the form of bending and yielding of structural members and E_i is the remaining energy available for impact.

The available impact energy can then be estimated from:

$$E_i = \frac{1}{2} M_1 \left(1 - \frac{M_1}{M_1+M_2}\right)(V_1 - V_2)^2 - E_d$$

For derailments, $E_d \cong 2.31 \times 10^6$ N.m

In order to relate available impact energy to penetration, Everett et al. (1971) established the following empirical relation:

$$F_i = 3.88 \times 10^{13} d^{1.5} \left(\frac{t}{D}\right)^3 \left(\frac{P_1 + P_o}{P_o}\right)^{0.6}$$

where F_i = impact force (N)

d = depth of penetration (m)

t = tank thickness (m)

D = head diameter (m)

P_1 = internal pressure (kPa)

P_o = ambient pressure (kPa)

The following equation was then assumed to relate impact force to impact energy:

$$E_i = F_i d$$

The critical penetration, d_c, for rupture was estimated from the Rosenblatt Method (1975):

$$d_c = \frac{0.1\ D\ \sigma_y\ \varepsilon_u}{M\ \varepsilon_y}$$

where σ_y = yield stress (kPa)

ε_y = yield strain

ε_u = ultimate strain

M = Modulus of Elasticity (kPa)

To determine the hole dimensions a geometric approach was taken. The method is crude but conservative when compared with observed incidents and tests (AAR, 1972). The geometry is shown in Figure 1. The hole will be elliptically shaped and is assumed to be oriented horizontally. Previous accidents have shown that the majority of punctures are contained within the dent.

The following equations were used to predict the hole length, L_h, and width, W_h :

$$L_h = \sqrt{R^2-(R-d)^2} \quad , \ d > d_c$$

$$W_h = 0.1 L_h \frac{d-d_c}{0.5-d_c}$$

The length was assumed to be equal to that of the dent. The width was assumed to be zero when the tank "just" fractures and 10% of the length at a penetration of 0.50 m, with a linear increase between. This assumption is consistent with observations of damage sustained by tanks in collision. At a penetration of 0.50 m, the modelled hole is large enough to allow the tank to empty in less than one minute. Finally, the area of the hole is:

$$A_h = \frac{\pi}{4} L_h W_h$$

RELEASE OF CARGO

Releases of liquefied gases from pressurized storage due to a breach in containment will be in the form of a two-phase jet. Further "flashing" will occur outside the tank due to the sudden pressure drop. The instantaneous discharge rate, Q (m^3/s), can be calculated from:

$$Q = \int dQ = \int u dA_h$$

where the velocity, u, is determined from the Bernoulli equation. For a hole in the head of a cylindrical tank:

$$Q = 2C_D \frac{L_h}{W_h} \int_{-W_h/2}^{W_h/2} \sqrt{\left(\frac{W_h}{2}\right)^2 - y^2}\ \sqrt{2g\left(H-y + \frac{P_1-P_c}{\rho g}\right)}\ dy$$

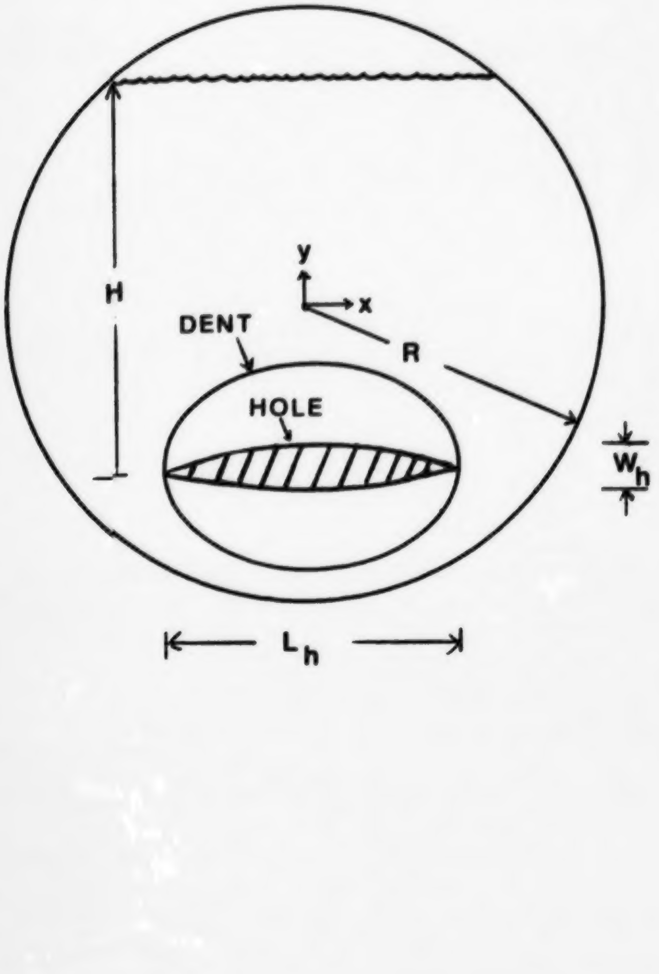
where C_D = discharge coefficient

g = acceleration due to gravity (m/s^2)

ρ = liquid density (kg/m^3)

FIGURE 1

IDEALIZED HOLE GEOMETRY


H
y
x
DENT
R
HOLE
W_h
L_h

P_i = internal tank pressure

P_c = "choke" pressure at the breach

The choke pressure at the breach, is calculated from:

$$P_c = P_1 \left(\frac{2}{\gamma+1} \right)^{\gamma/\gamma^{-1}}$$

where γ is the ratio of specific heats.

As material is released, the vapour space within the tank will increase causing liquid to boil thermodynamically at a rate m_e (kg/s).

Since Q will vary with time, a mass balance is required to obtain the relationship between the two:

$$\rho \frac{dV_L}{dt} = \rho Q + m_e$$

However, for an incremental volume:

$$dV_L = A_L \, dH$$

where A_L is the surface area of the liquid/vapour interface.
Assuming Q to be constant over small decreases in H, the required time can be calculated from:

$$\Delta t = \int_{t_2}^{t_1} dt = \int_{H_2}^{H_1} \frac{A_L}{Q + m_e/\rho} \, dH$$

For estimating m_e, Dodge et al. (1980) published the following empirical relation:

$$m_e = m_{es} - 1.9 \, m_{es}^{5/4} \Big/ \left[\rho A_L \sqrt{R_g T_1 / M_w} \right]^{\frac{1}{2}}$$

where m_{es} is the evaporation rate required to maintain saturation pressure at T_1, and is calculated from

$$m_{es} = \frac{P_1 M_w \Delta V_g / R_g T_1}{\Delta t}$$

The energy required to evaporate m_e is obtained from the remaining liquid as sensible heat and from heat transfer from the atmosphere. The energy balance is:

$$m_e \lambda = W_L \rho_P \frac{\Delta T}{\Delta t} + U_o A_o \nabla T_{Lm}$$

If the tank is insulated as in the case of chlorine tankers, $U_o = 0$. However, even for uninsulated tanks, heat transfer from the atmosphere had only a very minor effect. If T_2 is the final temperature within the tank after ΔT, then the pressure at that point, P_2, can be calculated from the Clausius-Clapeyron equation:

$$\ln \frac{P_2}{P_1} = \frac{M_w \lambda}{R_g} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

New temperature and pressure values have thus been generated for the next iteration.

The total fraction, f, of the release that flashes is assumed to do so adiabatically, and is calculated from the following enthalphy balance:

$$H_{L1} = fH_{V,bp} + (1-f)H_{L,bp}$$

RESULTS AND DISCUSSION

A set of numerical models have been developed to calculate the profile of the discharge rate from a breach in containment. The models have been developed on an IBM PC using IBM Basic. The model outputs (i) discharge rate split into liquid and vapour fractions, (ii) time, (iii) total volume spilled, (iv) tank pressure and temperature.

For liquefied gases transported under their vapour pressure, the discharge rate profile will depend on (i) hole size and location, (ii) discharge coefficient, (iii) cargo, and (iv) ambient temperature. Figures 2, 3 and 4 show how these parameters affect the discharge of material. The total volume spilled in all cases was 114 m^3.

From Figure 2 it can be seen that discharge rate is sensitive to kinetic energy. Once the tank material fails, it will tear much more easily.

In Figure 3, the effect of the nature of the contained material upon discharge rate is shown for the same collision conditions. The storage pressure accounts for the difference in profiles. Thus the lower the storage pressure is, the higher are the penetration and thus hole size, but the lower is the discharge rate. This same principle applies to Figure 4. However, it must be remembered that the lower the ambient temperature, the smaller the flash fraction.

All profiles can be fitted to a polynomial of the form:

$$Q = k_o + k_1 t + k_2 t^2 + k_3 t^3 + k_4 t^4$$

which becomes the source term for a heavy gas dispersion model. The coefficients reflect the parameters mentioned above. For pressurized releases, both vapour and liquid profiles require curve fitting since the flashing fraction decreases with time due to the decreasing bulk liquid temperature.

The expected trend in the magnitudes of the hazard zone is for different hole sizes as shown in Figure 5, and is based on the research for ocean carriers transporting LNG. Since for small holes, the hazard zones can be significantly smaller, it can be concluded that for an accurate risk assessment, the source term requires detailed quantification.

FIGURE 2

DISCHARGE RATE - TIME PROFILES VS IMPACT SPEED

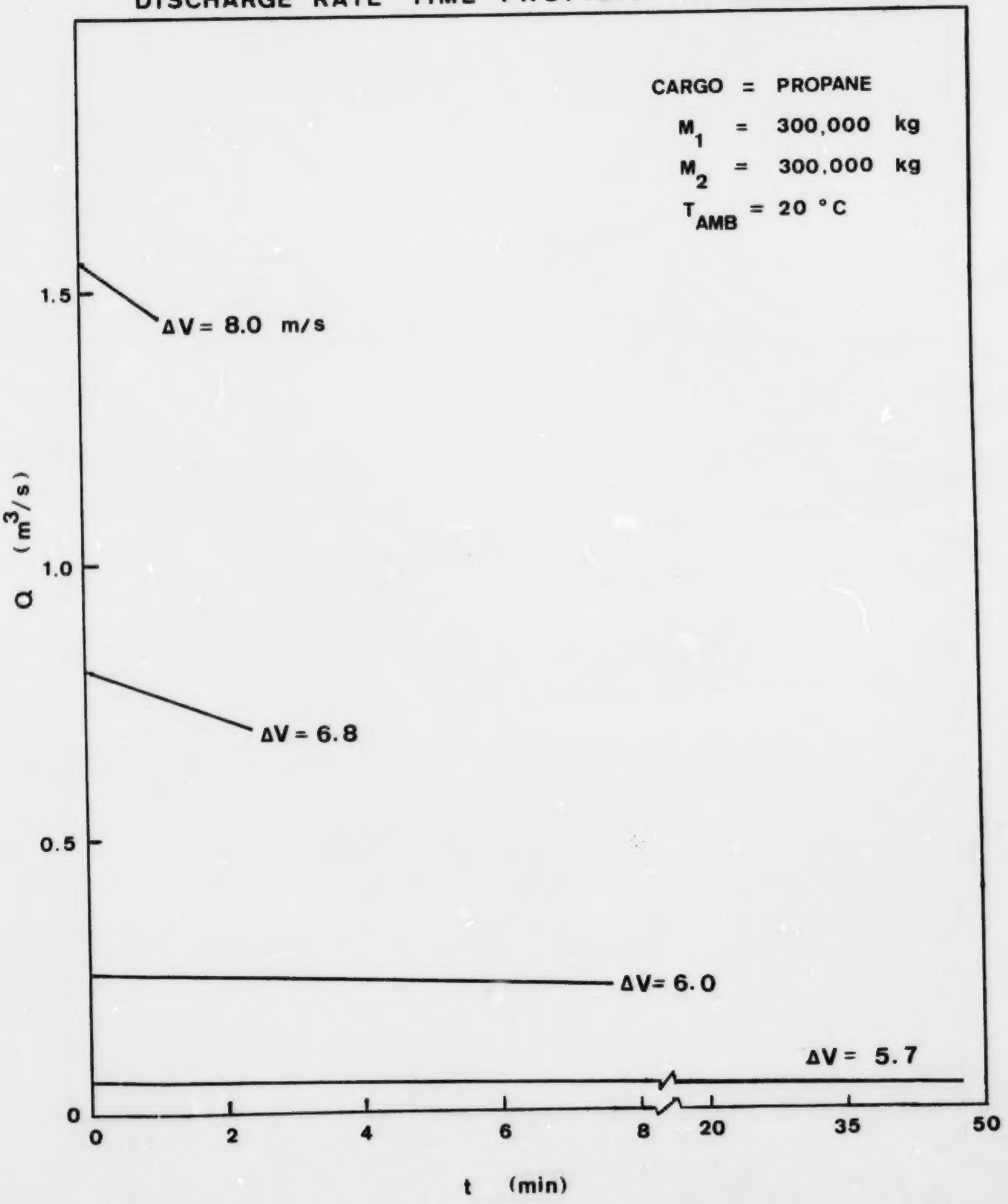


FIGURE 3

DISCHARGE RATE - TIME PROFILES FOR VARIOUS LIQUEFIED GASES

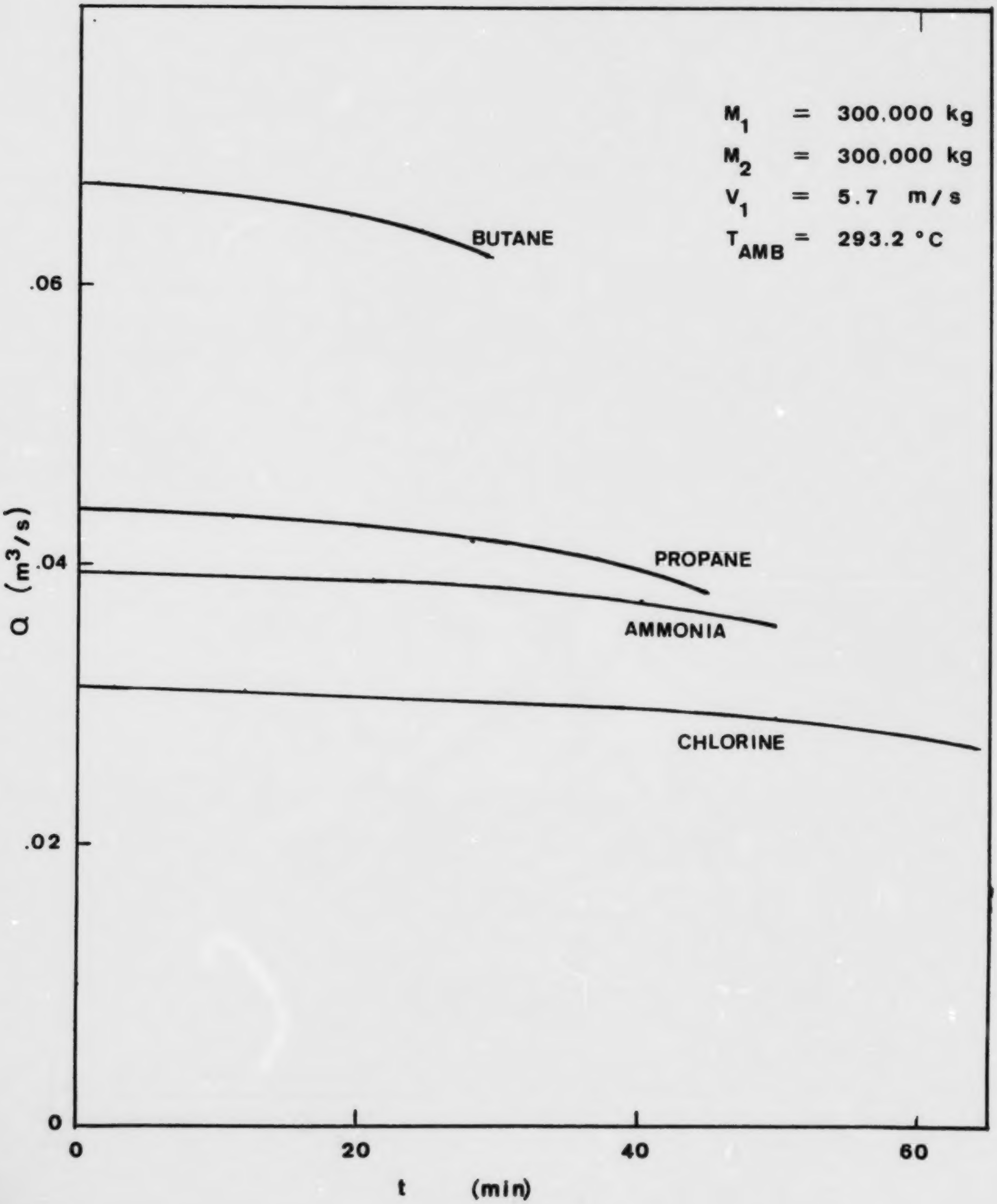


FIGURE 4

DISCHARGE RATE – TIME PROFILES VS AMBIENT TEMPERATURE

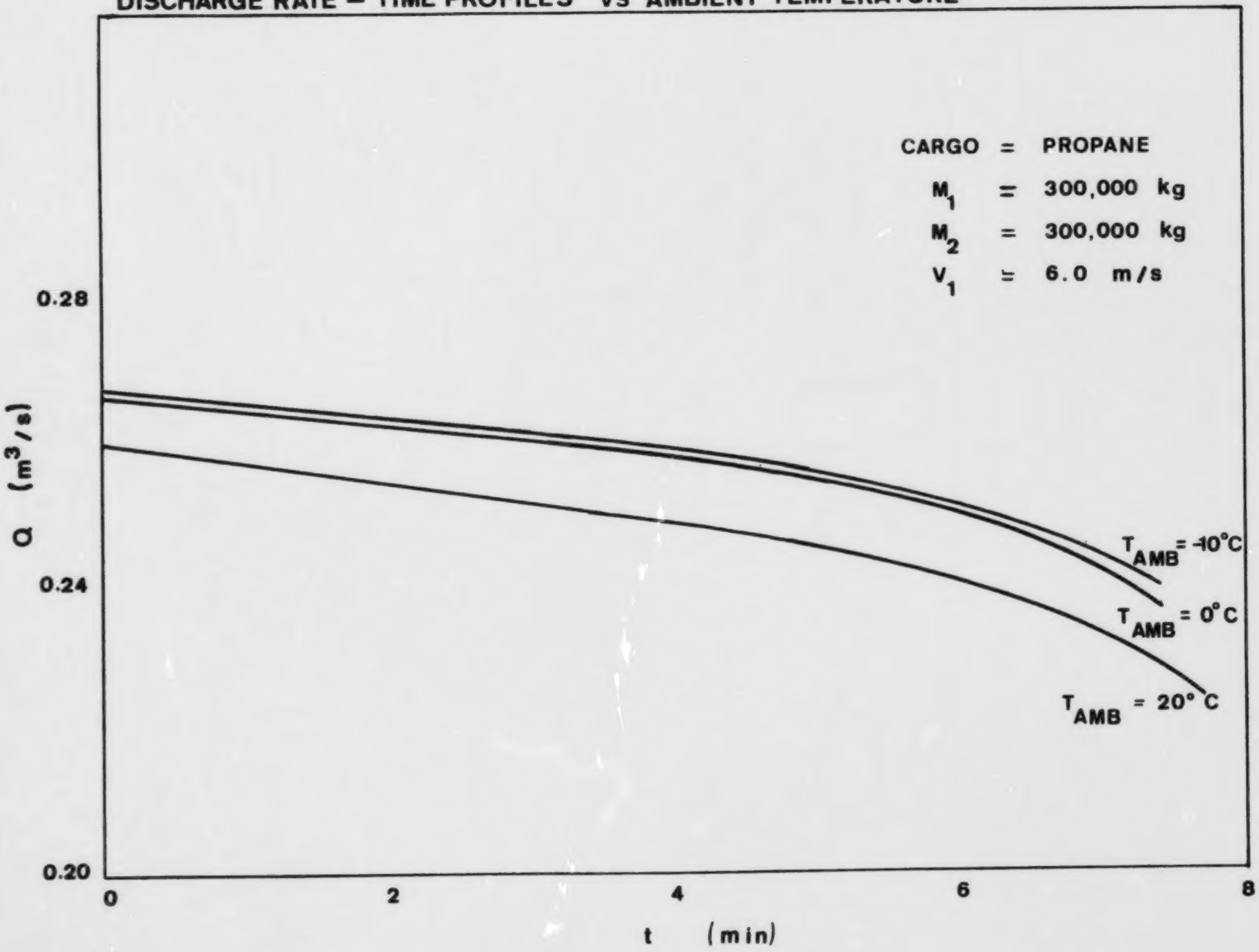
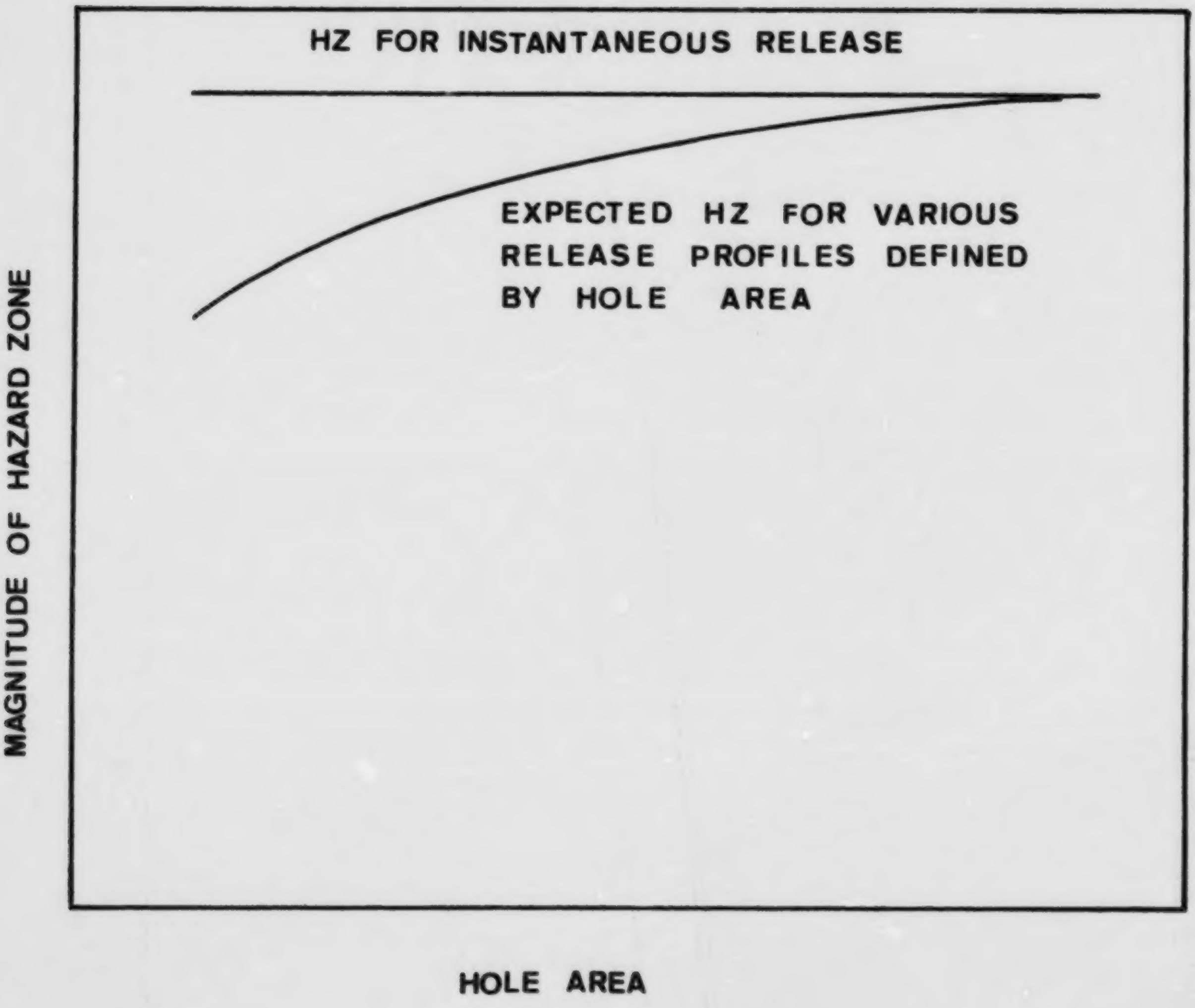


FIGURE 5

EXPECTED HAZARD ZONE (HZ)



LIST OF SYMBOLS

KE - Kinetic Energy (N.m)
M_1,M_2 - combined mass of striking and struck railcars (kg)
V_1,V_2 - average velocity of striking and struck railcars (m/s)
E_c - absorbed collisional energy (N.m)
E_d - dissipated energy (N.m)
E_i - available impact energy on head (N.m)
F_i - impact force (N)
d - depth of penetration (m)
t - tank head thickness
D - head diameter (m)
P_1 - internal tank pressure (kPa)
P_o - ambient pressure (kPa)
M - modulus of elasticity (kPa)
σ_y - yield stress (kPa)
ε_y - yield strain
ε_u - ultimate strain
R - tank radius (m)
L_L - hole length (m)
L_h - hole width (m)
A_h - hole area (m^2)
Q - discharge rate (m^3/s)
u - discharge velocity (m/s)
C_D - discharge coefficient
H - height of liquid head (m)
P_c - choke pressure (kPa)
g - acceleration due to gravity (m/s^2)
ρ - liquid density (kg/m^3)
γ - ratio of specific heat capacities
V_L - volume of liquid in the tank (m^3)
t - time (s)
m_e - evaporation rate within the tank (kg/s)
A_L - liquid/vapour interface area
R_g - gas law constant ($kPa.m^3/Kgmol.K$)
T_l - bulk liquid temperature in tank (K)
M_w - molecular weight
V_g - volume of vapour space in tank
λ - heat of vapourization (J/kg)
W_L - mass of liquid in tank (kg)
C_p - heat capacity of liquid (J/kg.K)
ΔT - Temperature difference = T_1-T_2 (K)
ΔT_{Lm} - log mean temperature difference (K)
U_o - overall heat transfer coefficient ($J/m^2.s.K$)
A_o - tank surface area (m^2)
H_{LI} - liquid enthalphy at storage temperature (J/kgmol)
$H_{L,bp}$ - liquid enthalphy at boiling point (J/kgmol)
$H_{V,bp}$ - vapour enthalphy at boiling point (J/kgmol)
f - fraction that flashes
y - position in the hole

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A PERSPECTIVE ON THE BEHAVIOUR OF CHEMICALS SPILLED IN SOIL

by

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INTRODUCTION

The purpose of this paper is to present a new perspective on the issue of soil contamination by chemicals. It is an unashamedly academic perspective, which it is hoped will bring some new insights and ideas into this increasingly important subject.

Chemicals enter soil from spills, from landfill and dump leachates, from leaking tanks and pipes, and by deliberate addition for agricultural or pest control purposes. They may also be present as a result of atmospheric deposition processes, thus even soils in "pristine" areas may be contaminated. In many cases the level of contamination is clearly unacceptable because the chemical can migrate into air which will be inhaled, into water which will be drunk, or into food which will be eaten. It may have profound ecological effects. Action is then required to decontaminate the soil, or at least to reduce the chemical concentrations to a tolerable level. The problem is "how do we do this?"

In the last three decades there have been massive developments in technology to decontaminate water and air. There are numerous texts on biological oxidation, filtration, scrubbing, absorbing, stripping, precipitation etc., especially from controlled sources. But there is little information about soil decontamination. Perhaps "soil treatment" is the next growth industry.

Air and water are fluids, thus the overwhelming preference when treating them is to induce them to flow to a stationary piece of equipment through which they pass and are subject to chemical removal. Soils are not (usually) fluids thus inducing them to move to the equipment is not nearly as easy. It can be done by excavating, transporting and, for example, incinerating, but the costs are often prohibitive. The process is very disruptive and can result in severe occupational exposure to the workers. Few localities relish being the dumping ground for contaminated solids.

Perhaps these brute force techniques can be replaced by more subtle interventions. There is increasing evidence that such intervention is possible and economical. In this paper we explore these possibilities.

In-situ or ex-situ?

The first question is "should we treat the soil in-situ, leaving it stationary, but inducing the chemical to move - or should we move the soil to a treatment facility?" Perhaps a guiding principle may emerge that in situ treatment is preferred and excavation should be viewed only as a last resort. To be more specific, perhaps a series or hierarchy of options is emerging in order of decreasing subtlety and desirability and increasing cost. These may be:

(1) Leave the soil alone to decontaminate naturally

(2) Intervene by in-situ enhancement of natural processes of decontamination

(3) Intervene by in situ treatment involving introduction of an artificial decontamination process

(4) When all else fails, remove the soil, treat it and return it to the

site.

If this approach is accepted, even in part, then it is essential to start with an appreciation of the condition of the chemical in the soil. Only if we understand its partitioning can we understand its natural fate. It is thus useful to digress to consider the chemical's condition as it exists in the soil.

CHEMICAL PARTITIONING AND TRANSPORT IN SOILS

We can regard soils as consisting of four phases, mineral matter (sand, clays etc.), organic matter (humic material etc.), water and air. The volume percentages could be respectively 65, 5, 10, 20, a typical bulk density being 1500 kg/m^3. When a chemical is introduced into this matrix it partitions between these phases as shown in Figure 1. The concentrations in each phase differ and are multiples or partition coefficients of each other. For example, the air-water partition coefficient is a Henry's Law Constant.

As the amount of chemical increases, the concentrations increase until a point of saturation is reached at which all phases simultaneously refuse to accept more chemical. Any additional chemical will form a separate "pure chemical" phase which may displace the air or water.

It is critically important to know which regime applies because the chemical behaviour in these regimes is quite different.

There are several methods of calculating these partitioning properties, but basically the approach is mass balancing subject to the partition coefficient constraints. Table 1 gives an example of such a partitioning calculation for benzene in a soil, the three conditions representing subsaturation, saturation and supersaturation with pure benzene present displacing some air.

Having established the condition of the chemical it may be possible to estimate the rates of the various transport and transformation processes to

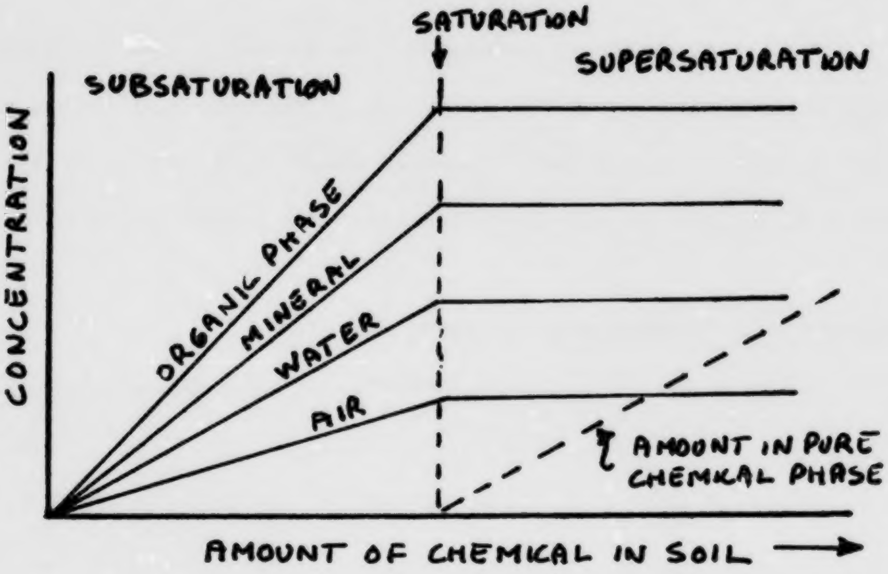

FIGURE 1 VARIATION OF PARTITIONING OF CHEMICAL IN SOIL

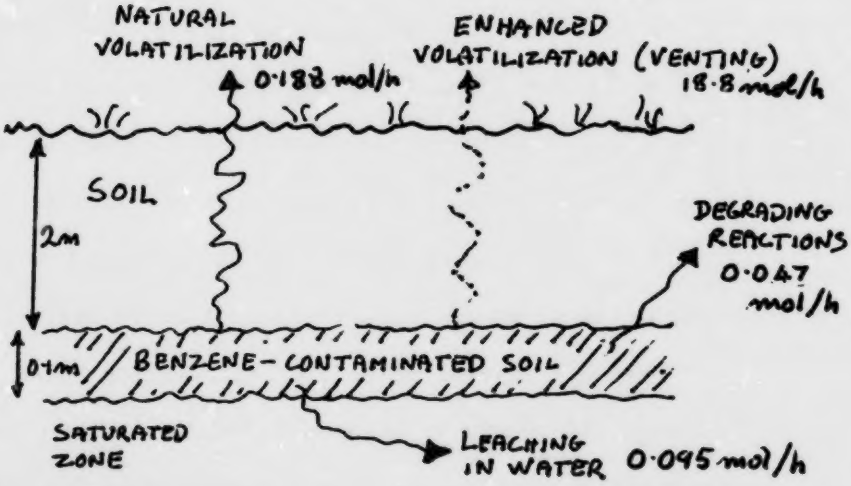
NATURAL VOLATILIZATION
0·188 mol/h
ENHANCED VOLATILIZATION (VENTING)
18·8 mol/h
SOIL
2m
DEGRADING REACTIONS
0·047 mol/h
0·1m
BENZENE - CONTAMINATED SOIL
SATURATED ZONE
LEACHING IN WATER
0·095 mol/h

FIGURE 2 ILLUSTRATION OF RELATIVE CHEMICAL FATES

SEE TABLE 1c FOR MORE DETAIL

TABLE 1A SUBSATURATED CONDITIONS

```
CHEMICAL DISTRIBUTION AND FATE

benzene/gasoline

PROPERTIES
MOLECULAR WEIGHT g/mol        78
SOLUBILITY g/m3               1780
VAPOR PRESSURE Pa             10000
VAPOR DENSITY g/m3            314.8244
LOG KOW & KOW                 2.13             134.8964
KOC                           55.30751
DENSITY kg/m3                 879

HALF LIFE HOURS & DAYS        48000            2000

AREA m2 100    THICKNESS OF CHEMICAL LAYER m .2    DEPTH IN SOIL m 2
AMOUNT kg 150       GRAMS 150000

CONDITION OF CHEMICAL IS    SUBSATURATED

               AIR          WATER        ORGANIC      MINERAL      CHEMICAL
DENSITIES      0.119E+01    0.100E+04    0.100E+04    0.220E+04    0.879E+03
VOLUMES        0.400E+01    0.200E+01    0.100E+01    0.130E+02    0.000E+00
Z VALUES       0.404E-03    0.228E-02    0.223E-01    0.228E-01    0.113E+01
CONC mol/m3    0.239E+01    0.135E+02    0.132E+03    0.135E+03    0.000E+00
CONC g/m3      0.186E+03    0.105E+04    0.103E+05    0.105E+05    0.000E+00
CONC ug/g      0.157E+06    0.105E+04    0.103E+05    0.479E+04    0.000E+00
MOLES          0.955E+01    0.270E+02    0.132E+03    0.175E+04    0.000E+00
GRAMS          0.745E+03    0.211E+04    0.103E+05    0.137E+06    0.000E+00
PERCENT        0.497E+00    0.140E+01    0.687E+01    0.912E+02    0.000E+00
              0.5% IN AIR  1.4% IN WATER 7% IN ORGANIC
FUGACITY (Pa)=              5914.093       MATTER     MOST (91%)
VOLUME OF CONTAMINATED SOIL m3             20         SORBED TO    NOTE
SOIL DENSITY kg/m3          1580.237                  MINERAL      ZERO
                                                        MATTER
PROCESS          D VALUES       FLUXES         PERCENTS
REACTION         0.469E-05      0.278E-01      0.142E+02
LEACHING         0.951E-05      0.562E-01      0.288E+02
VOLATILZATN      0.188E-04      0.111E+00      0.570E+02
TOTAL            0.330E-04      0.195E+00

OVERALL HALF LIFE hours & days               6829.036      284.5432

AIR DIFFUSION D VALUE                        1.87957E-05    9 MONTHS
WATER DIFFUSION D VALUE                      1.054331E-09
AIR BOUNDARY LAYER D VALUE                   .152243
EQUIVALENT AIR FLOW RATE m3/h                4.656456E-02


ENHANCED FATE WITH THE FOLLOWING FACTORS
VOLATILIZATION FACTOR  100
DEGRADATION FACTOR     1
LEACHING  FACTOR       1

PROCESS          D VALUES       FLUXES         PERCENTS
REACTION         0.469E-05      0.278E-01      0.248E+00
LEACHING         0.951E-05      0.562E-01      0.502E+00
VOLATILZATN      0.188E-02      0.111E+02      0.992E+02
TOTAL            0.189E-02      0.112E+02                    5 DAYS

OVERALL HALF LIFE hours & days               118.9989      4.958287
```

TABLE 1B SATURATED CONDITIONS

```
CHEMICAL DISTRIBUTION AND FATE

benzene/gasoline

PROPERTIES
MOLECULAR WEIGHT g/mol        78
SOLUBILITY g/m3               1780
VAPOR PRESSURE Pa             10000
VAPOR DENSITY g/m3            314.8244
LOG KOW & KOW                 2.13            134.8954
KOC                           55.30751
DENSITY kg/m3                 879

HALF LIFE HOURS & DAYS        48000           2000

AREA m2 100    THICKNESS OF CHEMICAL LAYER m .2    DEPTH IN SOIL m 2
AMOUNT kg 253.632      GRAMS 253632

CONDITION OF CHEMICAL IS          3ATURATED

              AIR           WATER         ORGANIC       MINERAL       CHEMICAL
DENSITIES     0.119E+01     0.100E+04     0.100E+04     0.220E+04     0.879E+03
VOLUMES       0.400E+01     0.200E+01     0.100E+01     0.130E+02     0.607E-06
Z VALUES      0.404E-03     0.228E-02     0.223E-01     0.228E-01     0.113E+01
CONC mol/m3   0.404E+01     0.228E+02     0.223E+03     0.228E+03     0.113E+05
CONC g/m3     0.315E+03     0.178E+04     0.174E+05     0.178E+05     0.879E+06
CONC ug/g     0.265E+06     0.178E+04     0.174E+05     0.809E+04     0.100E+07
MOLES         0.161E+02     0.456E+02     0.223E+03     0.297E+04     0.684E-02
GRAMS         0.126E+04     0.356E+04     0.174E+05     0.231E+06     0.533E+00
PERCENT       0.497E+00     0.140E+01     0.687E+01     0.912E+02     0.210E-03

FUGACITY (Pa)=                10000
VOLUME OF CONTAMINATED SOIL m3                20                   NEGLIGIBLE
SOIL DENSITY kg/m3            1580.237                             AMOUNT

PROCESS            D VALUES         FLUXES           PERCENTS
REACTION           0.469E-05        0.469E-01        0.142E+02
LEACHING           0.951E-05        0.951E-01        0.288E+02
VOLATILZATN        0.188E-04        0.188E+00        0.570E+02
TOTAL              0.330E-04        0.330E+00

OVERALL HALF LIFE hours & days                6829.051       284.5438

AIR DIFFUSION D VALUE                         1.87957E-05      9 MONTHS
WATER DIFFUSION D VALUE                       1.054331E-09
AIR BOUNDARY LAYER D VALUE                    .152243
EOUIVALENT AIR FLOW RATE m3/h                 4.656456E-02



ENHANCED FATE WITH THE FOLLOWING FACTORS
VOLATILIZATION FACTOR  100
DEGRADATION FACTOR       1
LEACHING  FACTOR         1

PROCESS            D VALUES         FLUXES           PERCENTS
REACTION           0.469E-05        0.469E-01        0.248E+00
LEACHING           0.951E-05        0.951E-01        0.502E+00
VOLATILZATN        0.188E-02        0.188E+02        0.992E+02     5 DAYS
TOTAL              0.189E-02        0.189E+02

OVERALL HALF LIFE hours & days                118.9992       4.958298
```

TABLE 1C APPROXIMATE SIMULATION OF CONNECTICUT SPILL

```
CHEMICAL DISTRIBUTION AND FATE

benzene/gasoline

PROPERTIES
MOLECULAR WEIGHT g/mol        78
SOLUBILITY g/m3               1780
VAPOR PRESSURE Pa             10000
VAPOR DENSITY g/m3            314.8244
LOG KOW & KOW                 2.13            134.8964
KOC                           55.30751
DENSITY kg/m3                 879

HALF LIFE HOURS & DAYS        48000           2000

AREA m2 100    THICKNESS OF CHEMICAL LAYER m .2    DEPTH IN SOIL m 2
AMOUNT kg 1500       GRAMS 1500000

CONDITION OF CHEMICAL IS    SUPERSATURATED

                 AIR           WATER         ORGANIC       MINERAL       CHEMICAL
DENSITIES        0.119E+01     0.100E+04     0.100E+04     0.220E+04     0.879E+03
VOLUMES          0.258E+01     0.200E+01     0.100E+01     0.130E+02     0.142E+01
Z VALUES         0.404E-03     0.228E-02     0.223E-01     0.228E-01     0.113E+01
CONC mol/m3      0.404E+01     0.228E+02     0.223E+03     0.228E+03     0.113E+05
CONC g/m3        0.315E+03     0.178E+04     0.174E+05     0.178E+05     0.879E+06
CONC ug/g        0.265E+06     0.178E+04     0.174E+05     0.809E+04     0.100E+07
MOLES            0.104E+02     0.456E+02     0.223E+03     0.297E+04     0.160E+05
GRAMS            0.813E+03     0.356E+04     0.174E+05     0.231E+06     0.125E+07
PERCENT          0.542E-01     0.237E+00     0.116E+01     0.154E+02     0.831E+02
                                                                     83%
FUGACITY (Pa)=                   10000
VOLUME OF CONTAMINATED SOIL m3              20
SOIL DENSITY kg/m3               1580.237

PROCESS             D VALUES        FLUXES           PERCENTS      14%
REACTION            0.469E-05       0.469E-01        0.142E+02
LEACHING            0.951E-05       0.951E-01        0.288E+02  29% (LEADS TO
VOLATILZATN         0.188E-04       0.188E+00        0.570E+02      GROUNDWATER
TOTAL               0.330E-04       0.330E+00                  57%    PROBLEMS)

OVERALL HALF LIFE hours & days                   40387.56     1682.815

AIR DIFFUSION D VALUE                            1.87957E-05
WATER DIFFUSION D VALUE                          1.054331E-09    4.6 YEARS
AIR BOUNDARY LAYER D VALUE                       .152243         HALF LIFE
EQUIVALENT AIR FLOW RATE m3/h                    4.656456E-02    IF LEFT ALONE


ENHANCED FATE WITH THE FOLLOWING FACTORS                          NOW
VOLATILIZATION FACTOR   100                                       NEGLIGIBLE
DEGRADATION FACTOR      1
LEACHING  FACTOR        1

PROCESS             D VALUES        FLUXES           PERCENTS     REDUCED TO
REACTION            0.469E-05       0.469E-01        0.248E+00    1MONTH BY
LEACHING            0.951E-05       0.951E-01        0.502E+00      ENHANCEMENT
VOLATILZATN         0.188E-02       0.188E+02        0.992E+02
TOTAL               0.189E-02       0.189E+02

OVERALL HALF LIFE hours & days                   703.7705      29.32377
```

which the chemical is subject. This problem has been tackled by Jury et al (1, 2, 3, 4) in an excellent series of papers in which an algebraic evaluative soil fate model has been developed. Recently we have simplified that model, with some loss of fidelity, to give a method of estimating loss by volatilization, leaching in water and reaction (5). It is also possible to include pure phase migration rate as an additional process, which is, of course, applicable only in the supersaturated regime. This is illustrated conceptually in Figure 2 for benzene.

Such assessments demonstrate three rather obvious principles.

1. If supersaturation conditions apply and the pure liquid phase is mobile and not appreciably water soluble, then the dominant method of transport is usually by pure phase flow or migration. Movement of the chemical in "solution" in air and water is usually relatively slower and can often be neglected. The free or pure phase liquid may tend to be drawn by capillary forces into the interstices or pores of the soil matrix, thus becoming immobilized. Continued flow of the free liquid thus leaves behind a residual volume of immobile liquid which may be very difficult to remove.

2. If subsaturation conditions apply the chemical can migrate only if an appreciable fraction (e.g. 0.1% or greater) of it is present in the mobile air or water phases and is thus subject to flow and diffusion.

3. Chemicals differ greatly in their partitioning characteristics in a manner dependent primarily on their vapour pressure and water solubility.

4. If the chemical is a mixture (as occurs with gasoline, fuel oils and many PCB fluids) the behaviour is more complex. The mixture's "solubility" and "vapour pressure" are presumably some weighted mean of the properties of the pure components, thus they depend on composition. As the liquid composition changes due to evaporation, dissolution and reaction, the composition and these properties change accordingly.

CHEMICAL TRANSFORMATION IN SOILS

It is possible to conduct experiments to determine the rates of chemical transformation in soils. Biodegradation is usually the dominant process, but rates of hydrolysis oxidation and even photolysis can be appreciable. The rate constants or half lives can also be incorporated into the fate model to give a perspective on the relative contributions of transport and transformation. The overall half life can be evaluated. This is illustrated in Figure 3 for benzene using an assumed degradation half life of 10 days.

Unfortunately, when pure phase is present the super-saturation conditions may often be too toxic for microorganisms to be effective. It is then necessary to wait for more dilute conditions to prevail before relying on biodegradation to be effective.

It is thus possible (in theory at least), to deduce the transport fate of the chemical in the soil and pose the question, "is allowing decontamination to proceed at its natural rate acceptable, i.e. is "do nothing" a reasonable option?" The answer is likely to be "yes" when natural soil biodegration rates are fast or when volatilization is rapid. If there is a possibility of groundwater or deep soil contamination the answer will probably be "no".

But at least the question should be asked.

INTERVENTION

Intervention to Enhance Natural Rates of Recovery

If natural decontamination processes are unacceptably slow and intervention is necessary, it seems likely that the best approach is to enhance the rates of those natural processes which result in mitigation. Nature is thus given a "helping hand" to accomplish in 1 month what may have taken 3 years naturally.

When a model of soil fate is available it is easy to explore the possibility of increasing the (mathematical) rates of the various transport and transformation parameters and determine how these enhancements accelerate recovery. For example, for benzene or gasoline spilled in the unsaturated zone in soil from a leaking underground storage tank, the obvious approach is to enhance volatilization by artificial soil venting.

In other cases, nutrients and aeration have been used to enhance natural biodegradation rates. In some cases it may be possible to remove chemicals by pumping water from the soil with natural or artificial replenishment. Several techniques are available to treat the water. The study of natural and enhanced chemical biodegradation in the subsurface environment, and in particular in groundwater, is the subject of increasing attention, but the literature remains sparse. An excellent recent review is that of Lee and Ward (6) which is part of a published symposium held in 1983 (7).

The key quantitative information is the factor by which the natural rate can be increased - is it 1.1 or 10 or 1000?

We return to this issue of enhanced recovery shortly giving an example of a successful remediation effort involving enhanced volatilization.

Intervention by Artificial Recovery

If enhanced recovery is not feasible or too slow the next option is to intervene by introducing a new mobile medium into the soil (in addition to air and water) and induce the chemical to migrate in it. For organic chemicals such as PCBs the obvious approach is to extract with a hydrocarbon such as kerosene. Other possibilities exist such as supercritical CO_2, surfactant solutions and even subsurface combustion. The petroleum industry is particularly expert at inducing reluctant organics to flow from the subsurface environment at depths of thousands of metres. It is puzzling that so little has been done on analogous technologies at a few metres depth.

The use of an innocuous liquid such as low aromatic content kerosene is particularly attractive for removal of chlorinated hydrocarbons with on site distillation and recycle. The residual in situ kerosene can be later biodegraded or evaporated.

Soil Removal and Decontamination

There is a growing literature on the excavation of soils, especially from landfill sites or dumps, and their treatment. The treatment methods include incineration using various configurations, extraction using various agents, treatment with various chemical agents such as acids, bases and oxidants. These processes have been reviewed recently by Rulkers and Assink (8).

The principal problems of removal are the disruption, exposure of workers and nearby residents to evaporated and of course the cost of the operation which can amount of hundreds of dollars per ton of soil. We suggest that in many cases it may be preferable to avoid the high intensity exposure events by more prolonged treatment by an in situ method.

AN EXAMPLE OF ENHANCED SOIL REMEDIATION

Approximately 500 U.S. gallons of unleaded gasoline were accidentally spilled into the unsaturated zone at a service station in Connecticut. The property was approximately 125 x 150 feet with a building and two pump islands. The site is shown in Figure 3 which also shows the general plume shape as determined by taking vapour samples from wells.

Excavation and soil removal would have been very disruptive and expensive. Fortunately, it proved possible to clean up the site with minimal disruption and cost by enhancing the rate of gasoline evaporation. This possibility was recognized because some laboratory soil column experiments had been done in which evaporation or venting had been simulated, thus establishing the feasibility of the approach.

The laboratory experiments conducted by Hoag et al (9) showed (Figure 4) that 99.0% of benzene could be removed from soil in 100 minutes. 3.3 L of air was required to remove 1 g of benzene. This benzene vapour concentration (300 g/m^3) corresponds at 20 C to 9400 Pa partial pressure which is close to the saturation vapour pressure. The rate of air withdrawal per unit area was 26 $cm^3/cm^2.min$ or a superficial velocity of 26 cm/min. Tests with gasoline were done at 23 to 160 cm/min (10, 11) at which all the gasoline was removed. The air/gasoline ratio was 16 to 26 L air/g gasoline for soils of 25 and 125 g gasoline per kg soil. Clearly it is feasible not only to remove gasoline by venting or enhanced evaporation, but it is also feasible to quantify the process. An equilibrium model was devised in which the gasoline was treated as a 52 hydrocarbon mixture and it was concluded that equilibrium conditions were approached in the soil-air-gasoline subsurface system.

At the spill site three six inch diameter vacuum soil venting wells each connected to 20 cfm vacuum pumps were used to remove gasoline spill in the soil. A cross-section of the monitoring and soil venting installation can be seen in Figure 5. A plan view showing the various monitoring and recovery systems, with a total vapor hydrocarbon contour plume map is shown in Figure 3. It was assumed that the outer boundaries of the gasoline product plume were within the 10 mg/L and 50 mg/L vapour phase hydrocarbon concentrations.

Cumulative volumes of gasoline recovered in the three venting wells using the in-site process are shown in Figure 6. More than 90 percent of the gasoline recovery by the venting system occurred during the first 60 days of operation. A total of 1376 L of gasoline was removed by the venting process. A total of 303 L of gasoline was removed by bailing from the recovery well over a 6 month period. Virtually no gasoline was recovered using an automated gasoline

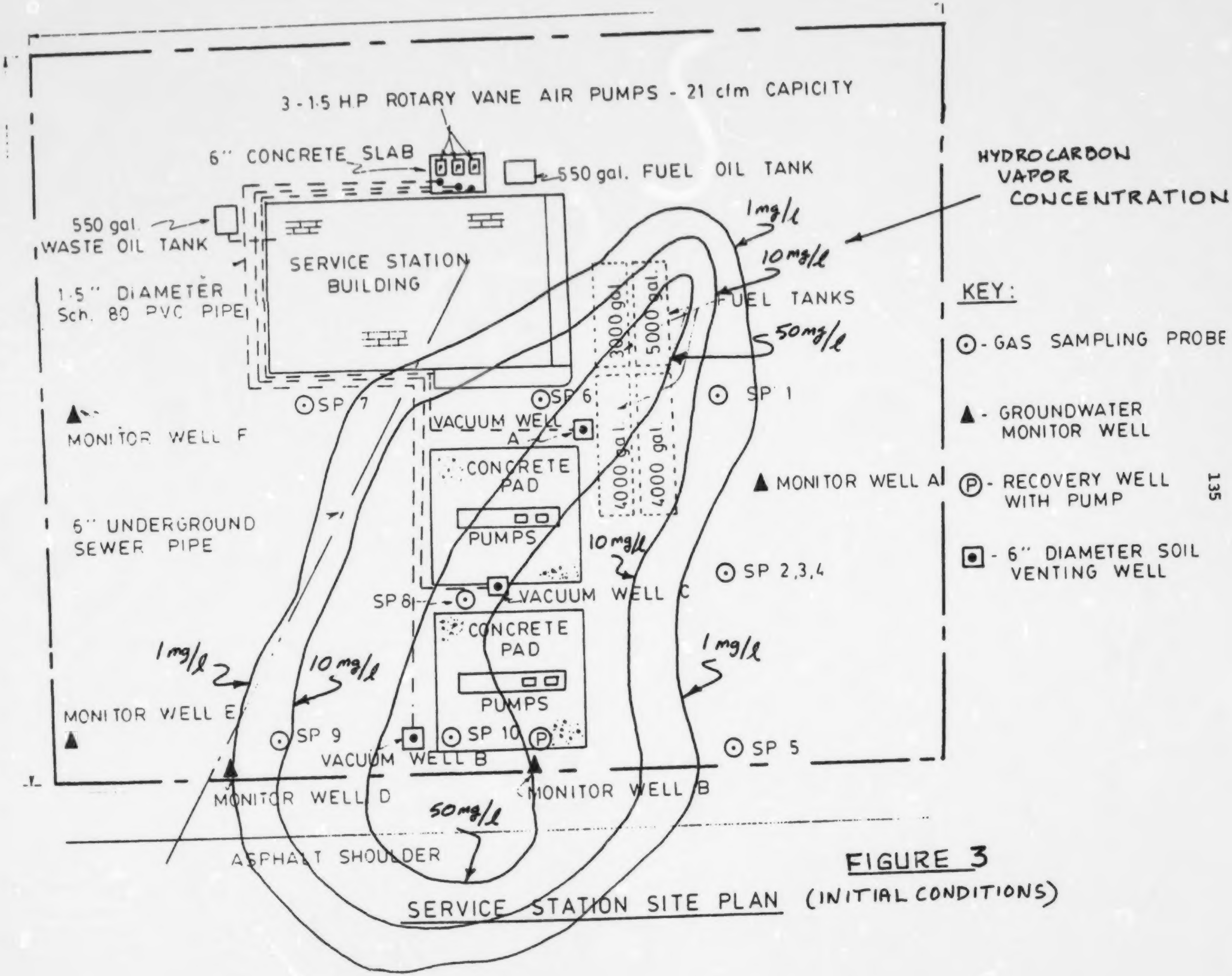
3 - 1.5 H.P ROTARY VANE AIR PUMPS - 21 cfm CAPICITY
6" CONCRETE SLAB
550 gal. FUEL OIL TANK
550 gal. WASTE OIL TANK
SERVICE STATION BUILDING
1.5" DIAMETER Sch. 80 PVC PIPE
MONITOR WELL F
6" UNDERGROUND SEWER PIPE
MONITOR WELL E
HYDROCARBON VAPOR CONCENTRATION
1mg/l
10mg/l
50mg/l
FUEL TANKS
3000 gal
5000 gal
4000 gal
4000 gal
SP 1
SP 6
SP 7
VACUUM WELL A
CONCRETE PAD
PUMPS
MONITOR WELL A
10mg/l
SP 2,3,4
SP 8
VACUUM WELL C
CONCRETE PAD
PUMPS
1mg/l
10mg/l
1mg/l
SP 9
SP 10
P
VACUUM WELL B
SP 5
MONITOR WELL D
MONITOR WELL B
50mg/l
ASPHALT SHOULDER
KEY:
⊙ - GAS SAMPLING PROBE
▲ - GROUNDWATER MONITOR WELL
Ⓟ - RECOVERY WELL WITH PUMP
⊡ - 6" DIAMETER SOIL VENTING WELL

FIGURE 3

SERVICE STATION SITE PLAN (INITIAL CONDITIONS)

Legend:

System Temperature = 20°C.

Induced Air Flow Rate = 0.3 l/min.

Initial Mass of Benzene Present = 9.0g.

Mass of Benzene Removed by Venting Process = 9.0g.

Benzene Vapor Phase Saturation Concentration = 320 mg/l;

o - Measured Values of Benzene Vapor Concentration.

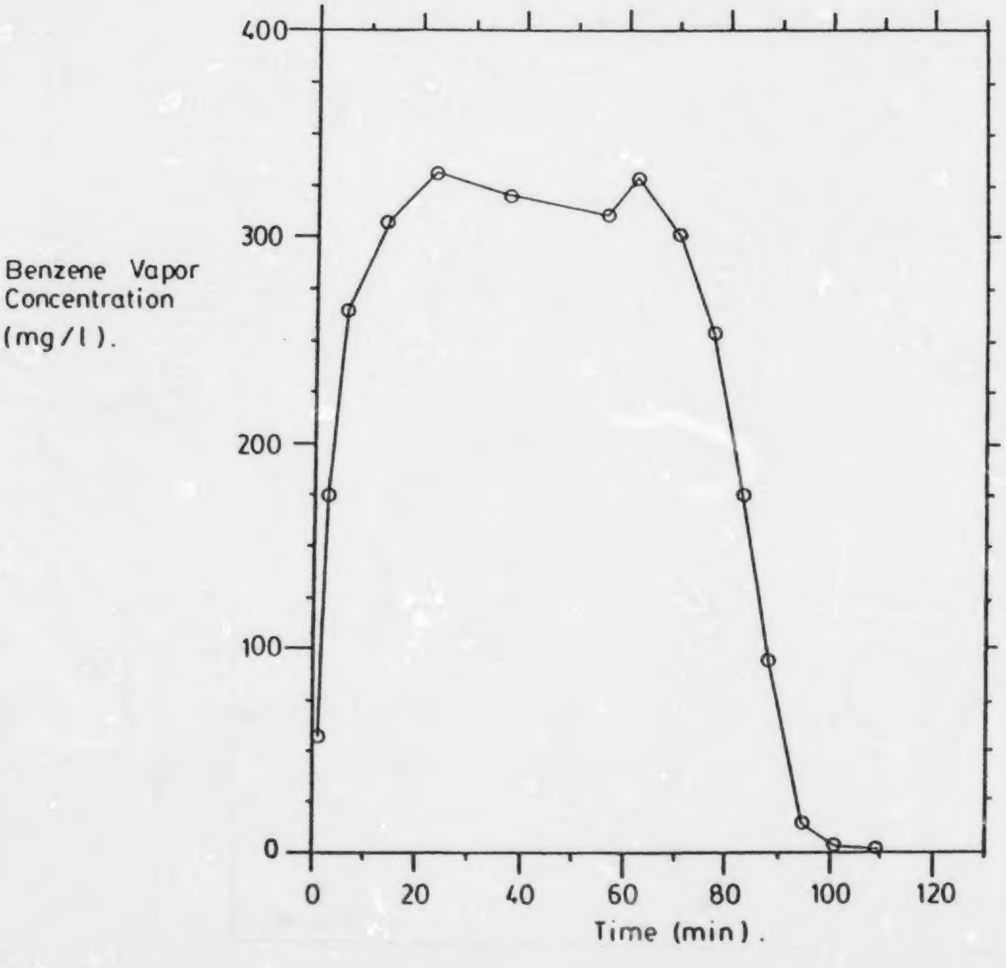

Figure 4: Trial Venting Run; Benzene Vapor Concentration Versus Time.

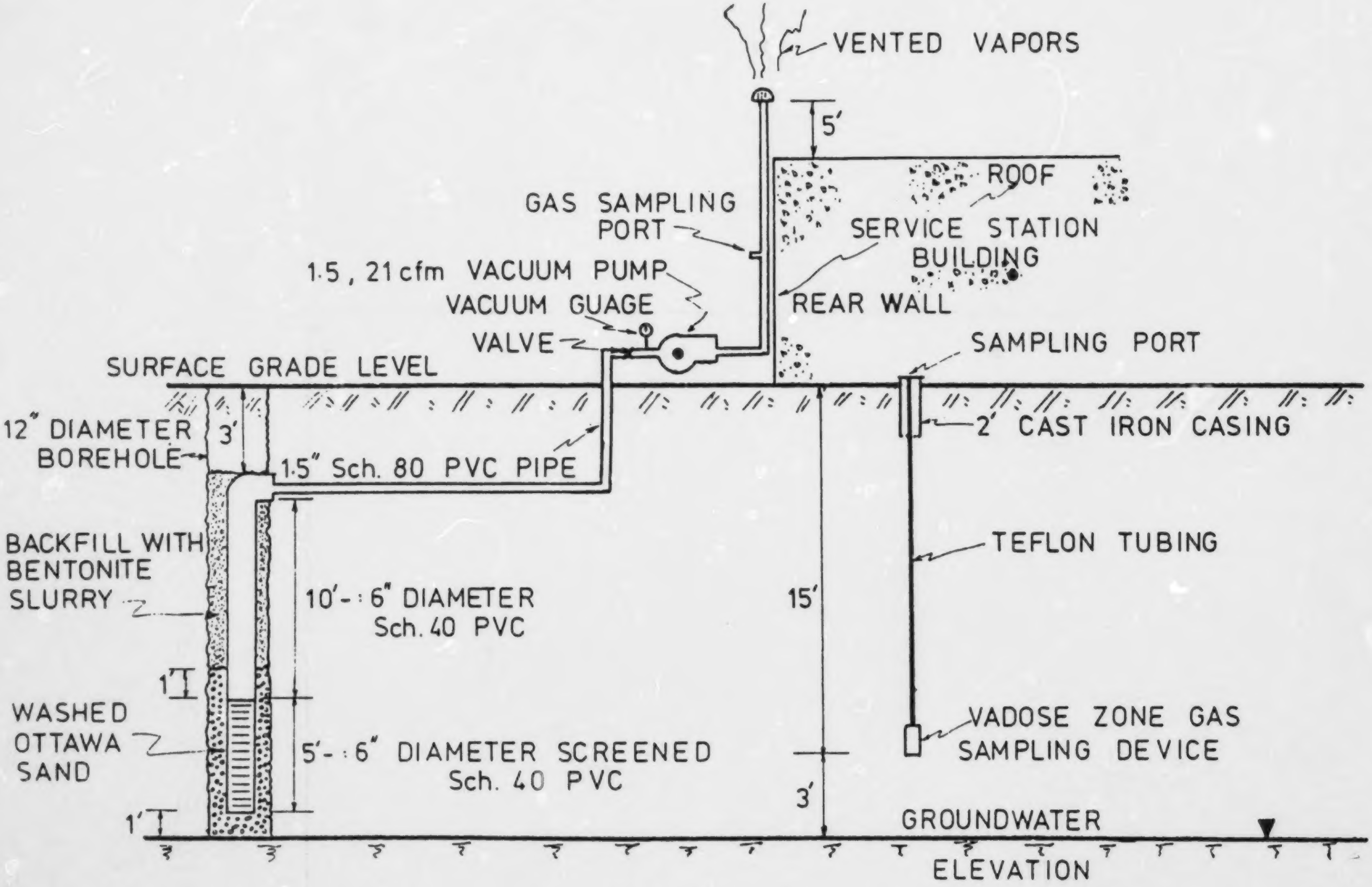
VENTED VAPORS
5'
ROOF
GAS SAMPLING PORT
SERVICE STATION BUILDING
1.5 , 21 cfm VACUUM PUMP
VACUUM GUAGE
REAR WALL
VALVE
SAMPLING PORT
SURFACE GRADE LEVEL
12" DIAMETER BOREHOLE
3'
2' CAST IRON CASING
1.5" Sch. 80 PVC PIPE
BACKFILL WITH BENTONITE SLURRY
TEFLON TUBING
10'- : 6" DIAMETER Sch. 40 PVC
15'
1'
WASHED OTTAWA SAND
VADOSE ZONE GAS SAMPLING DEVICE
5'- : 6" DIAMETER SCREENED Sch. 40 PVC
3'
1'
GROUNDWATER ELEVATION

FIGURE 5

SCHEMATIC PLAN FOR SOIL VENTING SYSTEM WITH GAS SAMPLING PROBES

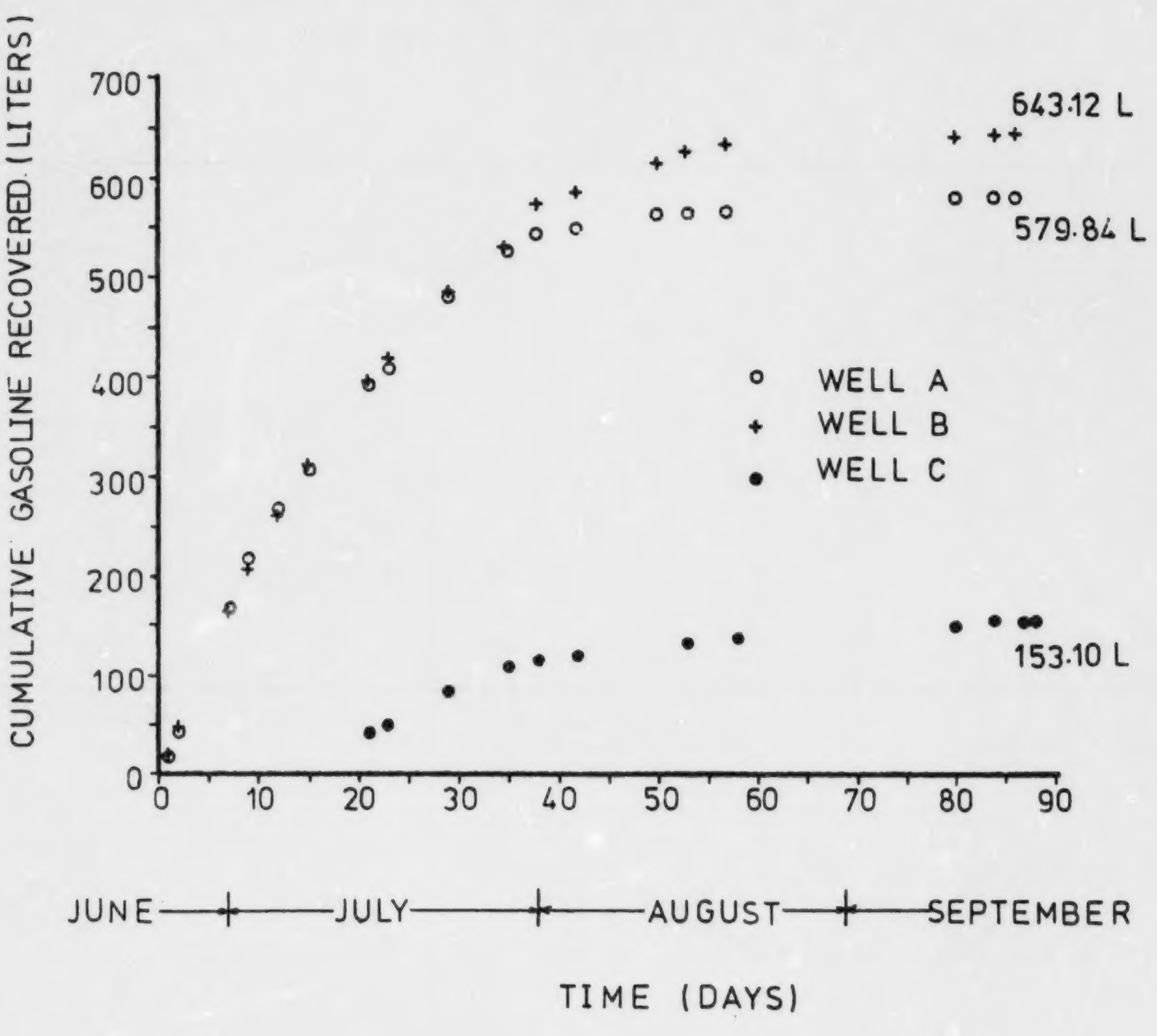

FIGURE 6
SOIL VENTING GASOLINE RECOVERY

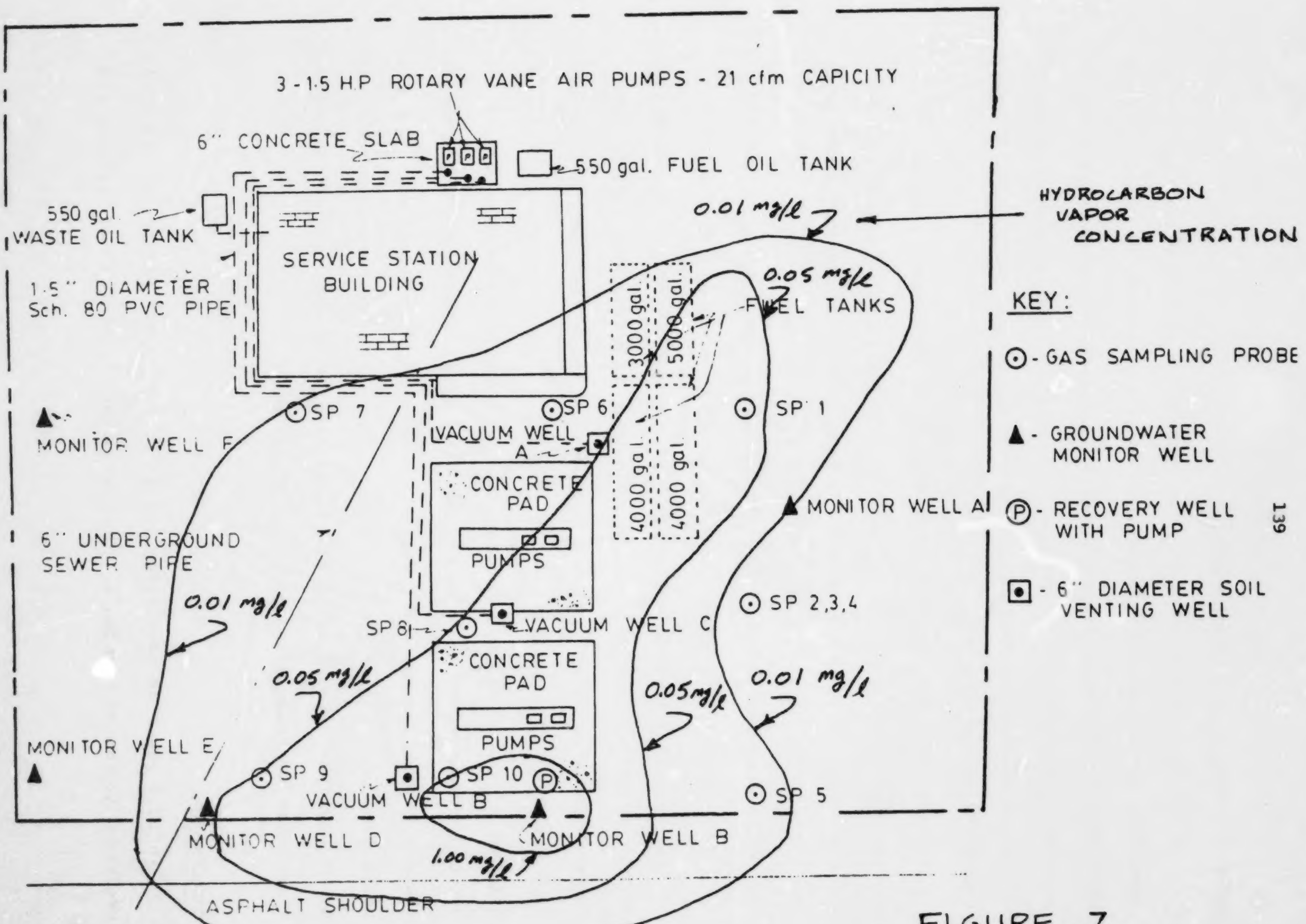
3 - 1.5 H.P ROTARY VANE AIR PUMPS - 21 cfm CAPICITY
6" CONCRETE SLAB
550 gal. FUEL OIL TANK
550 gal. WASTE OIL TANK
1.5" DIAMETER Sch. 80 PVC PIPE
SERVICE STATION BUILDING
HYDROCARBON VAPOR CONCENTRATION
0.01 mg/l
0.05 mg/l
FUEL TANKS
3000 gal.
5000 gal.
4000 gal.
4000 gal.
SP 7
SP 6
SP 1
MONITOR WELL F
VACUUM WELL A
CONCRETE PAD
PUMPS
MONITOR WELL A
6" UNDERGROUND SEWER PIPE
0.01 mg/l
SP 8
VACUUM WELL C
SP 2,3,4
CONCRETE PAD
0.05 mg/l
0.05 mg/l
0.01 mg/l
PUMPS
MONITOR WELL E
SP 9
SP 10
VACUUM WELL B
SP 5
MONITOR WELL D
MONITOR WELL B
1.00 mg/l
ASPHALT SHOULDER
KEY:
⊙ - GAS SAMPLING PROBE
▲ - GROUNDWATER MONITOR WELL
Ⓟ - RECOVERY WELL WITH PUMP
▣ - 6" DIAMETER SOIL VENTING WELL

FIGURE 7

SERVICE STATION SITE PLAN (FINAL CONDITION) scavenger pump in the recovery well.

After the first 60 days of soil venting the vapour phase hydrocarbon concentrations in the soil probes fell dramatically as shown in Figure 7. After 88 days of venting all hydrocarbon vapour concentrations were below 0.5 mg/L. At this time there was no detectable gasoline in any of the groundwater monitoring wells, whereas prior to soil venting several wells contained more than 2 feet of gasoline.

In the field soil venting system an areal withdrawal rate of air was designed and operated to be 31 cm^3/cm^2-min. The air to gasoline ration was 62 L air/g gasoline; about 3 times greater than experienced in laboratory under ideal conditions. The difference is probably attributable to failure to equilibrate the entire air flow, some "by-passing" or subsaturation occurring.

The remediation was thus successful from both the scientific and practical viewpoints. In 3 months the site had been substantially decontaminated. An obvious question is the issue of air pollution. No attempt was made to remove the gasoline from the air. If deemed necessary an absorber system could have been installed. Fortunately these hydrocarbons have a relatively short half life in air. It should be noted that excavation would also result in substantial evaporation and even an explosion hazard. If atmospheric dispersion characteristics are not favourable the system could be turned off. The air pollution disadvantages are considered to be small compared to the problems which could have resulted if the plume had spread out, and contaminated groundwater had reached the local water supply well.

CONCLUSIONS

In this paper we have attempted to present a new perspective on soil treatment to remove chemicals. This technology is still in its infancy and there is enormous scope for innovation. There is a certain inherent elegance in approaching soil treatment from the viewpoint of enhancing natural processes such as evaporation or biodegradation when possible. Clearly it is important to document the successes in the hope that these good examples will be copied. A key component of this enhancement is the "design" of the system in which quantitative expressions are developed using appropriate models, validated by laboratory and field data.

Further, we suggest that there is considerable scope for development of in situ interventions with solvents, surfactants and other treating agents and mechanisms. Perhaps a sequence of treatments may be optimal. Excavation and remote treatment may emerge as a "last resort", "brute force" approach. Undoubtedly the greatest challenge is the remediation of hazardous waste dump sites containing persistent toxic organic chemicals. Of particular concern are those sites which are close to valuable aquifers or waterways - the Niagara River being a prime example. No where is there greater need to seek remediation with subtlety.

Underlying this discussion is a growing appreciation that it is unacceptable to leave soils in a state of continued chemical contamination. The generation which caused the contamination (and therefore benefitted from it) has no right to pass on the cost, inconvenience and health risks to other generations. Encapsulation or barrier containment systems are inherently unsatisfactory. Surely we have an ethical obligation to pass on to others a biosphere, of which soils are a fundamental part, which is in a healthful uncontaminated condition?

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THE DEVELOPMENT OF A DISCIPLINED APPROACH FOR EMERGENCY RESPONSE

A METHODOLOGY FOR STRATEGIC DECISION MAKING DURING RESPONSE TO A CHEMICAL SPILL

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ABSTRACT:

Although the development of technical skills and tactics for response to a chemical emergency is of the utmost importance, one of the most critical aspects of the response is to have a methodology for decision making.

This paper will outline such a process, give a brief history on how it has been developed within the Canadian oil and chemical industries, and how it is gaining acceptance within these industries. The following four phases of a " **Disciplined Approach**" will be outlined:

- **SITUATION ANALYSIS**
- **DECISION ANALYSIS**
- **IMPLEMENTATION**
- **FEEDBACK**

giving a brief description of each. The importance of clear accurate communication between first responders, company and government representatives and technical advisors at the incident scene will be emphasized. The role the "**Disciplined Approach**" process can play in this communication and subsequent decision making will be highlighted.

INTRODUCTION:

Although environmental protection has always been important, an increased emphasis has been placed on protection of the environment with the passage of time. More effort has and will continue be devoted to improving the technology for dealing with chemical spills. The existence of this "Technical Seminar On Chemical Spills" sponsored by Environment Canada and other similar seminars for the sharing of technology sponsored by industry and government throughout Canada and the United States are evidence of this.

The number of people likely to be associated with a spill has also increased. In the past, the traditionally called upon fire and police departments were called to respond to emergencies, but today they are often joined by specially trained teams, response teams dispatched by the carrier, the shipper, and a number of representatives of numerous municipal, provincial and federal government agencies.

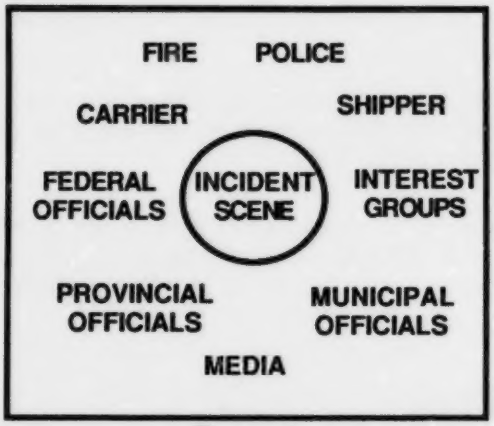


Figure 1

There is therefore an increasing complexity in responding to chemical emergencies. Some of the contributing factors are the growth in technology, and the number of individuals which must be dealt with at the incident scene. The decision making process at the incident scene must be capable of accommodating a large number of factors in a timely, efficient and effective manner. This decision process, like many of the issues which surround a hazardous materials incident must not be a complex one, on the contrary it must be simple and clearly understood by all participants responding to the emergency, and at the same time it must be capable of handling all the pertinent aspects of the incident.

I believe the **"Disciplined Approach to Emergency Response"** which I will present to you today will meet the criteria of a good emergency response decision making process. It is being presented for your consideration in the hopes that you may adopt its use as have an increasing number of response teams within the oil and chemical industry.

DEVELOPMENT:

The concept of teaching a **"Disciplined Approach to Emergency Response"** originated within Esso Chemical Canada.

The need for a program to specifically teach decision making skills to emergency responders within the company, was identified. The large number of products produced and used by the Imperial Oil organization, coupled with a complex transportation and distribution network operating over a wide geographic area, dictated the need for a good generic approach to decision making at the incident scene. We were challenged to find a program which was easily understood yet addressed the complexities of our products, the wide range of response locations and a multi modal distribution system.

Our initial training used a course developed by the National Fire Protection Association in the United States in co-operation with the U.S. Department of Transportation. The N.F.P.A. program was effective, but as time passed, ways became evident to improve it. The decision making process was lengthened beyond that taught by the N.F.P.A. by adding the elements of "final restoration" and "disposal of recovered or contaminated material". Further revisions were made to incorporate the Canadian Transportation of Dangerous Goods hazard classifications, and expand the scope of conditions and modes of transportation which may be encountered. The resources and techniques used to respond to an incident were expanded and changed to reflect those available in the Canadian situation. This includes the addition of external resources such as "CANUTEC" Transport Canada's emergency centre, "TEAP" the Canadian Chemical Producers' Association (CCPA) Transportation Emergency Assistance Plan, the mutual aid plan sponsored by the Western Canada Fertilizer Association and joint government industry plans such as JOSREP.

Over the past few years, the use of the **"Disciplined Approach"** training has expanded within the Imperial organization to the point where it has now been adopted as an integral part of the corporate "Major Spill Response Training".

Response to a major incident within Imperial will be provided by one of five "Major Spill Response Teams" located across Canada. Because these teams may be called upon to support each other it is important that training is consistent between the teams. To achieve this consistency an intensive five day course supplemented by response simulations, tests and individual training has been developed. It is at the five day course, which is jointly sponsored by Esso Resources Canada Limited, Esso Chemical and Esso Petroleum, where the **"Disciplined Approach"** is first taught and practised.

The CCPA who sponsor the "TEAP" mutual aid response network, have been one of the leaders in emergency response training in Canada. They have adopted the **"Disciplined Approach"** training as part of their Technical Advisor Training Course. These courses are attended by companies which represent the majority of the Canadian chemical industry.

The Canadian Chemical Producers' Association, in the interests of improving the overall quality of emergency response, promotes the development of training material for emergency responders through a "TEAP Training Sub Committee". Because of the demand for good training material by industry response teams, this committee has undertaken the development of a one day course on **"Disciplined Approach"** in co-operation with Lambton College in Sarnia. This joint development of course material, with an institution that is already noted for its emergency response courses, will help achieve two objectives.

(1) Provide quality ongoing training for chemical industry response team members, and

(2) Make the course material available to responders outside of the chemical industry.

DISCIPLINED APPROACH PROCESS:

The "Disciplined Approach" is a **data gathering** and **decision making** process to aid responders in handling an emergency in a logical and methodical manner.

The objective of the "Disciplined Approach" process is to **protect lives, property, and the environment in an efficient manner.**

The four basic steps in the process and their relationship to each other are shown below in figure 2.

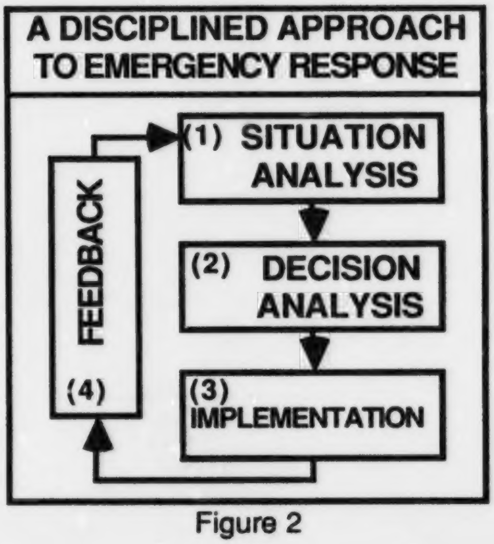


Figure 2

The process begins with the responder gathering data about the incident. This is known as the **situation analysis.** The information gathered is then processed by responders to make some critical decisions about the incident, this is known as the **decision analysis**. Once the decisions have been made, it is time to take action by implementing response to the incident through the use of the appropriate response **strategies and tactics.** The fourth and last part of the process is the feedback loop which evaluates the need to revise the response.

Let's take a brief look at each of the elements of the process.

SITUATION ANALYSIS

The **situation analysis** involves gathering information about:

- The problem
- The modifying conditions
- The potential losses
- The available resources

Three factors are considered in defining the problem. They are the stage of the incident, the harmful nature of the materials, and the type and condition of the shipping container.

Three factors are also considered in evaluating the modifying conditions. They are the location, the time, and the weather and climate conditions.

The potential losses are determined by assessing the exposure of life, the environment, or property to the existing or potential hazards involved in the incident.

The control measures are resources which may be called upon to respond to the incident from your company response team as well as external resources.

DECISION ANALYSIS

The **decision analysis** includes formulating a clear definition of

- **The critical issues**

and formulation and prioritizing :

- **Preventive strategies**
- **Corrective strategies**

and the selection of the appropriate **tactics** to implement the strategies.

Determining the **critical issues** is the heart of the "Disciplined Approach'. The **critical issues** normally consist of a list of lives, environment or property which must be protected from the hazards involved in the incident.

Preventive strategies are those strategies which will be implemented to rescue or protect people, and protect exposures, they include containment strategies, extinguishing ignited materials, and action taken to prevent container failure.

Corrective strategies are those which are implemented to clean up, and restore the affected area and dispose of contaminated product and debris.

IMPLEMENTATION

The **implementation** phase of the process consists of putting into action the **preventive and corrective strategies** to address the **critical issues** in order of priority. It should be emphasized that the **protection of life** is always the most important priority, this includes the protection of the community as well as the members of the response team. The **tactics** which were previously selected are employed to implement the **strategies**.

FEEDBACK

The **feedback** loop is the last but very important phase of the **"Disciplined Approach"**. It requires an ongoing reassessment of the process to ensure nothing has happened which would require a change in implementing the response to the incident. A transportation emergency is often a dynamic scene thus making it necessary to periodically reassess the action taken to respond to the incident and adjust the response in view of changing conditions.

The complete "Disciplined Approach" chart is included as attachment 1 at the end of this paper illustrating the process in greater detail.

BENEFITS OF DISCIPLINED APPROACH

Clearly the most important benefit to be derived from using the **"Disciplined Approach"** in responding to an incident is the **unification of the responders and government officials** in achieving a common objective. The process provides a common decision making model on which all involved parties can focus, thus decreasing the probability of conflicting priorities and views as to how the incident should be handled.

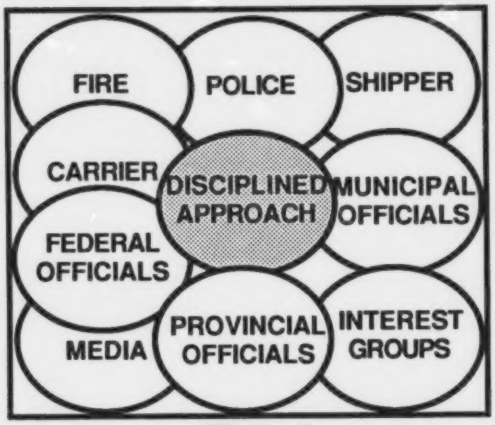


Figure 3

The all-too-common delays and conflicts which arise because of uncertainties or disputes about who is in charge of the response should be significantly minimized, if the parties can concentrate on the decision making process, instead of disputing who has the authority to make the decision.

After using the **"Disciplined Approach"** on industry responses and training simulations the following benefits are clearly evident:

- Increased understanding of the critical issues results when all responders are using the same process.

- The logical, simple nature of the process makes it easy to understand and use.

- The checklist ensures relevant factors are not overlooked.

- The process provides assistance in setting priorities.

- The process promotes more effective and efficient use of response resources.

- The process results in an increased level of safety for response team members and the general public.

DISCIPLINED APPROACH TRAINING:

As the **"Disciplined Approach"** has achieved wider use, the training methods for teaching it have likewise improved. As with any good training program, the **"Disciplined Approach"** training has always included interactive sessions where the trainees participate in the sessions. The exercises include completion of the situation analysis and decision analysis phases of the process while working in small groups after reading a case study and viewing slides presented during the training session.

Subsequest training is achieved through classroom simulations, in field exercises, and in tests of the emergency network. The process has proved to be a good training aid for team members when used to critique response to actual incidents during the post mortem review.

To assist in the training program considerible attention has been given to summarizing the **"Disciplined Approach"** in chart form. Two charts have been developed; one for incorporation in emergency response manuals and a second a 3' X 4' color wall chart for mounting in command centres. These charts are particularly useful in quickly explaining the process to officials and responders who may not yet be familiar with the process.

A number of possibilities to enhance the **"Disciplined Approach"** training have been identified and some of these are now being pursued either within Imperial or within the chemical industry. Some of the possibilities are:

- Development of improved case studies for use in the training sessions.

- Incorporation of Video tape presentations .

using these methods is to improve the feedback on individual comprehension of the course material, and evaluate proficency in using the process.

There are no doubt more ways to improve the **"Disciplined Approach"** training than we have identified here. Input from the seminar attendees would be much appreciated and can be forwarded to either of the authors of the paper.

CONCLUSIONS:

In summary, response to a chemical transportation emergencies is growing in complexity because of increased use of improved technology and the growing number of people who may be involved among other factors. To ensure prompt efficient response to emergencies, it is necessary to have a logical methodical means of gathering the pertinent information, analyzing it to determine the critical issues and prioritizing the strategies and tactics which will be used to respond to the emergency. The **"Disciplined Approach"** process is one which enables responders and other concerned parties to concentrate on the critical issues. Use of the **"Disciplined Approach"** by training responders, before they are called upon to deal with an incident will help make the response a more efficient effective one.

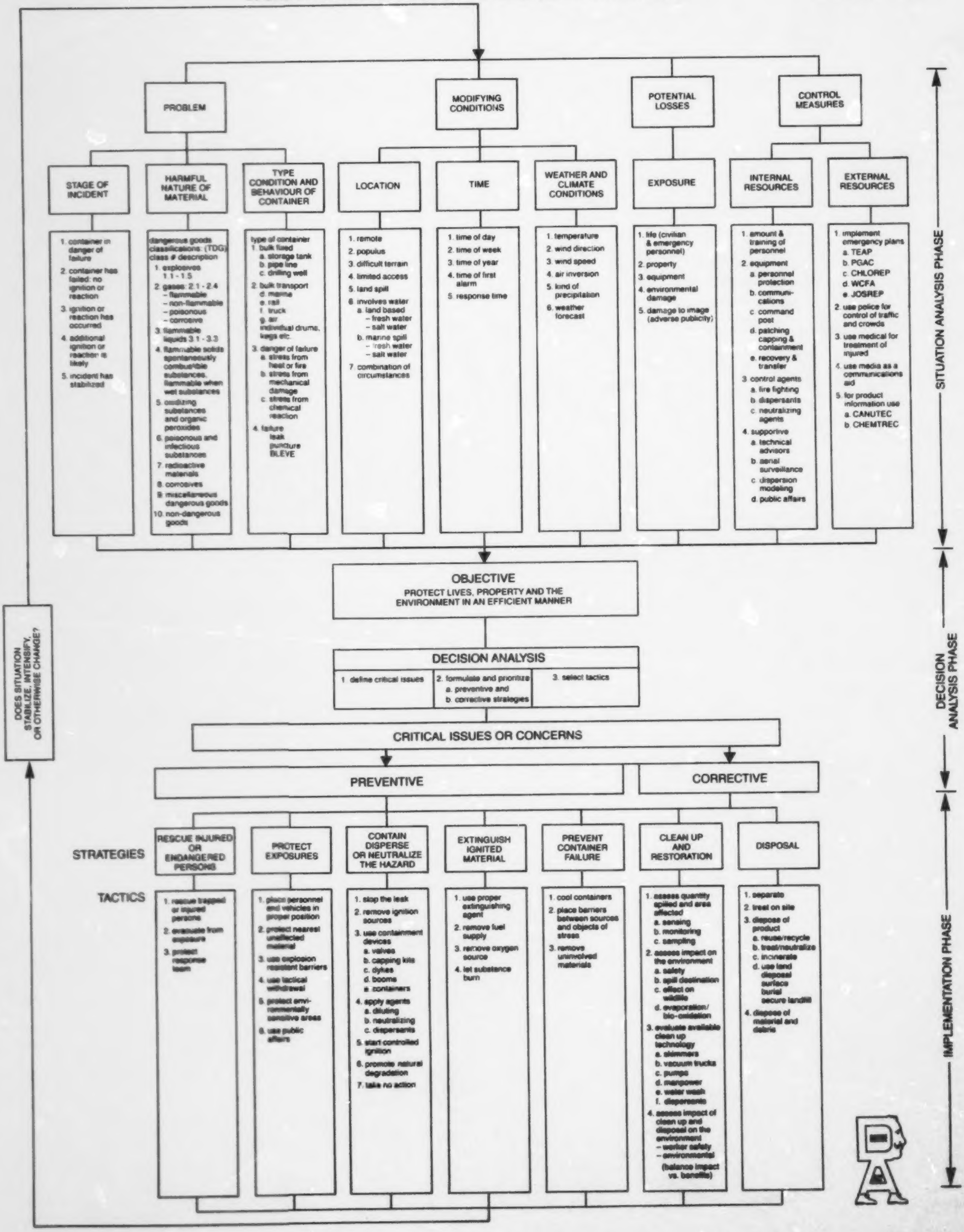
ACKNOWLEDGMENTS:

The authors wish to thank our companies for allowing the presentation of this paper. We also thank the National Fire Protection Association for the emergency response training materials developed by them which formed the basis for the development of the the "Disciplined Approach to Emergency Response" training program.

ATTACHMENT 1

THE CANADIAN CHEMICAL PRODUCERS' ASSOCIATION

A DISCIPLINED APPROACH TO EMERGENCY RESPONSE


PROBLEM
MODIFYING CONDITIONS
POTENTIAL LOSSES
CONTROL MEASURES
STAGE OF INCIDENT
1. container in danger of failure
2. container has failed: no ignition or reaction
3. ignition or reaction has occurred
4. additional ignition or reaction is likely
5. incident has stabilized
HARMFUL NATURE OF MATERIAL
dangerous goods classifications: (TDG) class # description
1. explosives 1.1 - 1.5
2. gases: 2.1 - 2.4
– flammable
– non-flammable
– poisonous
– corrosive
3. flammable liquids 3.1 - 3.3
4. flammable solids spontaneously combustible substances, flammable when wet substances
5. oxidizing substances and organic peroxides
6. poisonous and infectious substances
7. radioactive materials
8. corrosives
9. miscellaneous dangerous goods
10. non-dangerous goods
TYPE CONDITION AND BEHAVIOUR OF CONTAINER
type of container
1. bulk fixed
a. storage tank
b. pipe line
c. drilling well
2. bulk transport
d. marine
e. rail
f. truck
g. air
individual drums, kegs etc.
3. danger of failure
a. stress from heat or fire
b. stress from mechanical damage
c. stress from chemical reaction
4. failure
leak
puncture
BLEVE
LOCATION
1. remote
2. populus
3. difficult terrain
4. limited access
5. land spill
6. involves water
a. land based
– fresh water
– salt water
b. marine spill
– fresh water
– salt water
7. combination of circumstances
TIME
1. time of day
2. time of week
3. time of year
4. time of first alarm
5. response time
WEATHER AND CLIMATE CONDITIONS
1. temperature
2. wind direction
3. wind speed
4. air inversion
5. kind of precipitation
6. weather forecast
EXPOSURE
1. life (civilian & emergency personnel)
2. property
3. equipment
4. environmental damage
5. damage to image (adverse publicity)
INTERNAL RESOURCES
1. amount & training of personnel
2. equipment
a. personnel protection
b. communi-cations
c. command post
d. patching capping & containment
e. recovery & transfer
3. control agents
a. fire fighting
b. dispersants
c. neutralizing agents
4. supportive
a. technical advisors
b. aerial surveillance
c. dispersion modeling
d. public affairs
EXTERNAL RESOURCES
1. implement emergency plans
a. TEAP
b. PGAC
c. CHLOREP
d. WCFA
e. JOSREP
2. use police for control of traffic and crowds
3. use medical for treatment of injured
4. use media as a communications aid
5. for product information use
a. CANUTEC
b. CHEMTREC
SITUATION ANALYSIS PHASE
OBJECTIVE
PROTECT LIVES, PROPERTY AND THE ENVIRONMENT IN AN EFFICIENT MANNER
DECISION ANALYSIS
1. define critical issues
2. formulate and prioritize
a. preventive and
b. corrective strategies
3. select tactics
DECISION ANALYSIS PHASE
DOES SITUATION STABLIZE, INTENSIFY, OR OTHERWISE CHANGE?
CRITICAL ISSUES OR CONCERNS
PREVENTIVE
CORRECTIVE
STRATEGIES
TACTICS
RESCUE INJURED OR ENDANGERED PERSONS
1. rescue trapped or injured persons
2. evacuate from exposure
3. protect response team
PROTECT EXPOSURES
1. place personnel and vehicles in proper position
2. protect nearest unaffected material
3. use explosion resistant barriers
4. use tactical withdrawal
5. protect envi-ronmentally sensitive areas
6. use public affairs
CONTAIN DISPERSE OR NEUTRALIZE THE HAZARD
1. stop the leak
2. remove ignition sources
3. use containment devices
a. valves
b. capping kits
c. dykes
d. booms
e. containers
4. apply agents
a. diluting
b. neutralizing
c. dispersants
5. start controlled ignition
6. promote natural degradation
7. take no action
EXTINGUISH IGNITED MATERIAL
1. use proper extinguishing agent
2. remove fuel supply
3. remove oxygen source
4. let substance burn
PREVENT CONTAINER FAILURE
1. cool containers
2. place barriers between sources and objects of stress
3. remove uninvolved materials
CLEAN UP AND RESTORATION
1. assess quantity spilled and area affected
a. sensing
b. monitoring
c. sampling
2. assess impact on the environment
a. safety
b. spill destination
c. effect on wildlife
d. evaporation/ bio-oxidation
3. evaluate available clean up technology
a. skimmers
b. vacuum trucks
c. pumps
d. manpower
e. water wash
f. dispersants
4. assess impact of clean up and disposal on the environment
– worker safety
– environmental
(balance impact vs. benefits)
DISPOSAL
1. separate
2. treat on site
3. dispose of product
a. reuse/recycle
b. treat/neutralize
c. incinerate
d. use land disposal surface burial secure landfill
4. dispose of material and debris
IMPLEMENTATION PHASE

APPLICATIONS DE LA TECHNOLOGIE DES MEMBRANES DANS L'OUEST CANADIEN

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INTRODUCTION

La compagnie de chemin de fer Canadien National, la Région de l'Ouest et du Nord du Service de la Protection de l'Environnement (SPE) ainsi qu'une compagnie ayant des activités en pétrochimie ont indiqué à la Division des Techniques d'Intervention d'Urgence du SPE leur désir d'utiliser l'unité mobile d'osmose inverse (OI) dans l'ouest canadien pour fins de démonstrations et/ou d'essais. Les objectifs fixés furent de déterminer et/ou démontrer l'efficacité avec laquelle l'osmose inverse peut traiter les eaux contaminées suivantes:

- eau de lavage de wagons contenant de la potasse (CN)
- solution d'insecticides/herbicides (SPE)
- eaux de lixiviation d'un site d'enfouissement de produits chimiques (industrie pétrochimique)
- rejet industriel liquide (industrie pétrochimique).

Les essais ont eu lieu au cours de l'été 1985.

HISTORIQUE

- Le Canadien National a un important site de lavage de wagons de potasse à Melville (Saskatchewan). L'eau de lavage qui y est produite s'écoule dans un marais où elle s'évapore. Cette eau contaminée contient des quantités importantes de solides dissous totaux, plusieurs anions et cations (surtout chlorure et potassium) de l'ammoniaque, des nitrates et démontre un haut niveau de demande biologique d'oxygène. Ce marais, dépendamment des conditions atmosphériques, déborde et contamine l'environnement. Conscient du problème, le CN a demandé notre aide afin de déterminer si l'osmose inverse pourrait être utilisée pour traiter leur eau de lavage.

- L'Alberta utilise beaucoup d'insecticides et d'herbicides sur son territoire. Plusieurs fermiers achètent des barils contenant les produits chimiques en question et les utilisent pour différentes tâches dans leur travail. Certaine ville comme Edmonton rince à grande eau les barils une fois qu'ils sont vides afin de s'assurer qu'il n'y a plus aucune trace de produits toxiques. Ces eaux de rinçage sont normallement emmagasinées dans des réservoirs souterrains ou envoyées dans des sites d'enfouissement spécialisés. Les coûts qu'impliquent ces opérations sont très élevés sans compter les risques environnementaux. La Région de l'Ouest et du Nord du SPE intéressée par le problème en est venue à suggérer l'osmose inverse comme une solution possible. Un essai a donc eu lieu afin de tester notre unité mobile sur cette eau contaminée.

- Une compagnie ayant des activités en pétrochimie et qui désire demeurer dans l'anonymat a expérimenté, au cours des années, quelques problèmes dans deux domaines particuliers.

Premièrement: La compagnie qui possède un site d'enfouissement de produits chimiques, recueille de façon continue les eaux de lixiviation qui s'en échappent. Ces eaux contiennent une grande variété de contaminants organiques et inorganiques. Sachant que l'osmose inverse avait été efficace lors d'un essai effectué au site d'enfouissenent de Gloucester (Ontario) en 1984, il a été suggéré que cette méthode pourrait être une solution possible.

Deuxièmement: Une eau de rejet d'un procédé industriel qui est envoyée directement dans l'environnement contient parmi plusieurs autres molécules organiques et inorganiques du glycol monoéthylènique et du sodium. Un essai fût organisé afin de déterminer si l'osmose inverse pouvait séparer ces deux composés et concentrer le glycol afin de minimiser l'impact environnemental.

1. LA COMPAGNIE DU CANADIEN NATIONAL (Melville, Sask.)

A. Description des essais et résultats

L'essais de Melville a duré 4 jours (18, 19, 20 juin de même que le 2 juillet).

Le 18 juin, l'unité mobile d'osmose inverse fût configurée afin d'avoir quatre cylindres à haute pression en parallèle, chacun contenant deux membranes en série (voir Tableau 1). L'unité fût installée près du marais où les eaux de lavage s'écoulent. Nous avons par la suite conditionné les membranes à 200 lb/po^2 pour 1 heure, 400 lb/po^2 pour 15 minutes puis 600 lb/po^2 pour environ 1 heure. Au cours de cette journée, nous avons expérimenté des problèmes mineurs avec la pompe d'alimentation. Tout était fin prêt pour débuter officiellement l'essai le jour suivant.

TABLEAU 1

MEMBRANES D'OSMOSE INVERSE UTILISEES A MELVILLE LES 18 ET 19 JUIN 1985

PORT #	TYPE*	PRESSION MAXIMALE (lb/ po^2)	STRUCTURE
1	TORAY SP110	800	polyéther-polysulphone
2	DSI B441**	800	polyamide-polysulphone
3	UOP 4600***	600	polyéther/polyamide-polysulphone
4	FILMTEC FT-30	800	polyamide-polysulphone

* Toutes les membranes étaient de configuration enroulée et faites de films polymériques fins.

** DSI = Desalination Inc.

*** UOP = United Oil Product

Le 19 juin, l'unité fût mise en marche vers 8.00 AM et opérée à une pression de 600 lb/po^2 et un rapport de concentration de 1:1 pendant une heure. A 9.00 AM nous avons pris notre première série d'échantillons. Les résultats sont présentés au Tableau 2. Après quelques heures d'opération nous avons expérimenté d'autres problèmes avec la pompe d'alimentation. L'unité fût donc arrêtée pour environ 3 heures afin de permettre la réparation de la pompe. A 2:30 PM, l'unité était mise en marche de nouveau et opérée à 600 lb/po^2 et 3:1 pour une demi-heure. C'est alors qu'une deuxième série d'échantillons fût prélevée (Tableau 3). Les débits de solutions purifiées* mesurés au cours de la journée sont présentés au Tableau 4.

Le 20 juin nous avons continué notre essai sur le marais. L'unité fût configurée afin d'avoir les six cylindres à haute pression séparés en deux groupes parallèles, chacun contenant 6 membranes en série (6 Toray SP110 et 6 Filmtec FT-30). Nous voulions déterminer quel serait le débit de solution purifiée obtenu avec la nouvelle configuration de même que la qualité de cette eau lorsque produite à 800 lb/po^2. Les membranes furent conditionnées à 400 lb/po^2 pour 30 minutes, 600 lb/po^2 pour 15 minutes et enfin 800 lb/po^2 pour 15 minutes. A 800 lb/po^2 et 1:1 une série d'échantillons fût prélevée alors que le débit combiné des solutions purifiées était de 20 litres/minute. Les résultats obtenus sont présentés au Tableau 6. Ces échantillons ayant été prélevés aux ports d'échantillonnage #2 et #3 de notre unité, représentent les solutions purifiées les plus "sales" possibles (Il a été trouvé plus tard qu'un caoutchouc en "O" usé a causé une contamination partielle de la solution purifiée des membranes Toray SP110. C'est pourquoi les résultats obtenus pour ces membranes ne sont pas aussi bons que prévus). Les débits mesurés sont restés stables à 20 litres/minute pour plus d'une heure. Par après nous avons calibré l'unité afin d'obtenir un rapport de concentration de 4:1. A peine quelques minutes plus tard le débit combiné tombait à 15 litres/minute (dépôts sur les membranes). Nous avons décidé de mettre fin à cette portion de l'essai et nous nous sommes rendus à un endroit où l'eau de lavage était beaucoup plus contaminée par la potasse. Malheureusement, étant donné les problèmes déjà mentionnés que nous avons eu avec la pompe d'alimentation, nous étions en retard sur notre horaire et avons donc dû remettre au 2 juillet cette dernière portion de l'essai.

Le 2 juillet nous étions de retour à Melville. L'unité fût configurée afin d'avoir quatre cylindres à haute pression en parallèle, chacun contenant deux membranes en série. Le Tableau 1 présente les membranes utilisées avec l'exception de UOP 4600 qui a été remplacée par UOP 1001 capable de travailler jusqu'à 800 lb/po^2 de pression. Au cours de notre absence le Canadien National avait accumulé 500 gallons d'eau de potasse concentrée. Il était convenu que nous étions pour recirculer cette eau en système fermé afin que l'essai puisse durer environ 2 heures. La température initiale du réservoir étant de 29°C nous avons minimisé la duré du conditionnement des membranes (30 minutes) afin que la température n'augmente pas trop dû à la recirculation. Les débits enrégistrés au cours de l'essais sont présentés au Tableau 5. Nous pouvons remarquer qu'à 3:1 il y a début d'encrassement des membranes. Une première série d'échantillons fût prélevée à 800 lb/po^2 1:1 et une seconde, une demie-heure plus tard à 800 lb/po^2 3:1. Les résultats sont présentés aux Tableaux 7 et 8. La température à la fin de l'essais était de 37°C.

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* Voir annexe A

TABLEAU 2

RESULTATS D'OSMOSE INVERSE POUR MELVILLE (19 juin)

Conditions: 600 lb/po^2, 1:1 (Marais)

ANALYSES		RESULTATS					
TYPES	UNITES	SOLUTION CONTAMINEE	MEMBRANES (SOLUTION PURIFIEE)				SOLUTION CONCENTREE
			TORAY	DSI	UOP 4600	FILMTEC	
"Propriétés physiques"							
Conductivité	μS/cm	18400	506	2922	3464	724	+50000
Température	C	20	28	22	21.9	21.5	30
pH	pH	8.3	10	9.1	8.4	9.6	8.5
Alkalinité Totale	mg/l	653	80	69	50	50	738
Dureté Totale	mg/l	2790	4	60	8	4	5760
Solides dissous totaux	mg/l	18914	254	2170	2320	505	59696
"Ions Majeurs"							
Calcium	mg/l	380	2	10	2	2	728
Magnésium	mg/l	447	1	9	1	1	957
Potassium	mg/l	5600	85	730	960	195	12600
Sodium	mg/l	1600	27	215	187	48	3525
Bicarbonate	mg/l	797	0	35	51	0	791
Chlorure	mg/l	8300	88	1090	1300	224	18600
Sulphate	mg/l	1640	10	32	10	10	3600
Fer	mg/l	1	0.1	0.1	0.1	0.1	1.6
Manganèse	mg/l	.59	.06	.05	.04	.04	.73
"Paramètres Organiques"							
Azote Kjeldahl (N)	mg/l	110	12.5	22.5	1.8	12.5	140
Ammoniaque (N)	mg/l	16.5	10	14	22.5	8.25	33.5
Nitrate (NO3)	mg/l	90	8	25	14	10	140
Phosphate Total	mg/l	5.5	.25	.5	.25	.25	7.25
Phosphate Ortho	mg/l	3	.01	.02	.01	.02	1.25
DBO	mg/l	49	1	1	1	1	98

TABLEAU 3

RESULTATS D'OSMOSE INVERSE POUR MELVILLE (19 juin)

Conditions: 600 lb/po^2, 3:1 (Marais)

ANALYSES		RESULTATS					
TYPES	UNITES	SOLUTION CONTAMINEE	MEMBRANES (SOLUTION PURIFIEE)				SOLUTION CONCENTREE
			TORAY	DSI	UOP 4600	FILMTEC	
"Propriétés physiques"							
Conductivité	μS/cm	18400	677	24860	4400	1858	N/A
Température	C	20	29.5	35	29	31.2	31
pH	pH	8.3	10.1	9	8.8	9.4	8.5
Alkalinité Totale	mg/1	653	88	163	57	68	763
Dureté Totale	mg/1	2790	4	304	16	4	6120
Solides dissous totaux	mg/1	18914	304	11998	3235	1325	45322
"Ions Majeurs"							
Calcium	mg/1	380	2	66	5	2	792
Magnésium	mg/1	447	1	34	1	1	1006
Potassium	mg/1	5600	110	4200	1280	420	14600
Sodium	mg/1	1600	33	1250	274	137	3850
Bicarbonate	mg/1	797	0	89	28	7	797
Chlorure	mg/1	8300	122	6100	1610	700	20000
Sulphate	mg/1	1640	10	114	10	10	4080
Fer	mg/1	1	0.1	0.1	0.1	0.1	1.2
Manganèse	mg/1	.59	.04	.1	.05	.04	.74
"Paramètres Organiques"							
Azote Kjeldahl (N)	mg/1	110	20	40	45	20	175
Ammoniaque (N)	mg/1	16.5	11.25	32.5	34	15	74
Nitrate (NO3)	mg/1	90	5	90	17	23	130
Phosphate Total	mg/1	5.5	.5	.25	.5	.25	7.5
Phosphate Ortho	mg/1	3	.01	.03	.01	.01	1.5
DBO	mg/1	49	1	1	1	1	95

TABLEAU 4

DEBITS DE SOLUTION PURIFIEE POUR LES DIFFERENTES MEMBRANES D'OSMOSE INVERSE (19 juin, Melville)

PORT #	TYPE DE MEMBRANE	DEBITS (sec/L)	
		1:1	3:1
1	2 X TORAY SP110	40	43
2	2 X DSI B441	20	18
3	2 X UOP 4600	16	18
4	2 X FILMTEC FT-30	26	27

TABLEAU 5

DEBITS DE SOLUTION PURIFIEE POUR LES DIFFERENTES MEMBRANES D'OSMOSE INVERSE (2 juillet, Melville)

PORT #	TYPE DE MEMBRANE	DEBITS (sec/L)	
		1:1 (30°)	3:1 (37°)
1	2 X TORAY SP110	19	40
2	2 X DSI B441	13	23
3	2 X UOP 1001	19	41
4	2 X FILMTEC FT-30	16	40

TABLEAU 6

RESULTATS D'OSMOSE INVERSE POUR MELVILLE (20 juin)

Conditions: 800 lb/po^2, 1:1 (Marais)

ANALYSES		RESULTATS			
TYPES	UNITES	SOLUTION CONTAMINEE	MEMBRANES (SOLUTION PURIFIEE)		SOLUTION CONCENTREE
			TORAY*	FILMTEC	
"Propriétés physiques"					
Conductivité	μS/cm	2658	3229	356	+50000
Température	C	21.2	22	22.5	24
pH	pH	8.6	8.8	9.9	8.3
Alkalinité Totale	mg/l	402	58	50	706
Dureté Totale	mg/l	3280	64	4	6320
Solides dissous totaux	mg/l	25106	2495	279	50121
"Ions Majeurs"					
Calcium	mg/l	422	16	2	832
Magnésium	mg/l	540	6	1	1030
Potassium	mg/l	8400	860	96	16000
Sodium	mg/l	2140	278	27	4175
Bicarbonate	mg/l	388	39	0	861
Chlorure	mg/l	11200	1250	126	23000
Sulphate	mg/l	1950	14	10	4200
Fer	mg/l	1	.4	.1	1.5
Manganèse	mg/l	.35	.04	.04	.73
"Paramètres Organiques"					
Azote Kjeldahl (N)	mg/l	87.5	2	20	150
Ammoniaque (N)	mg/l	43.5	8.5	6.75	79.5
Nitrate (NO3)	mg/l	66	16	3	98
Phosphate Total	mg/l	5.25	.75	.5	9
Phosphate Ortho	mg/l	1.5	0.25	.025	2
DBO	mg/l	8	2	2	70

* Contamination dû à un caoutchouc en "O" usé.

TABLEAU 7

RESULTATS D'OSMOSE INVERSE POUR MELVILLE (2 juillet)

Conditions: 800 lb/po^2, 1:1 (Réservoir)

ANALYSES			RESULTATS			
TYPES	UNITES	SOLUTION CONTAMINEE	MEMBRANES (SOLUTION PURIFIEE)			
			TORAY	DSI	UOP 1001	FILMTEC
"Propriétés physiques"						
Conductivité	µS/cm	36800	2000	5640	670	1460
Température	C	N/A	30	32	32	32
pH	pH	6.2	5.8	6	4.5	5.9
Alkalinité Totale	mg/l	1230	170	160	0	100
Dureté Totale	mg/l	1880	4	44	4	44
Solides dissous totaux	mg/l	25709	1257	3628	322	870
"Ions Majeurs"						
Calcium	mg/l	512	2	10	2	13
Magnésium	mg/l	146	1	5	1	3
Potassium	mg/l	11600	570	1700	158	410
Sodium	mg/l	360	24	58	4	14
Bicarbonate	mg/l	1501	207	195	0	122
Chlorure	mg/l	11300	456	1660	170	348
Sulphate	mg/l	290	10	10	10	10
Fer	mg/l	17	.1	.5	.1	.6
Manganèse	mg/l	6.1	.06	.28	.26	.13
"Paramètres Organiques"						
Azote Kjeldahl (N)	mg/l	237.5	17.5	20	15	15
Ammoniaque (N)	mg/l	32.5	4.75	12.25	6.25	4.75
Nitrate (NO3)	mg/l	1	1	1	1	1
Phosphate Total	mg/l	50	0.25	.25	0.25	1
Phosphate Ortho	mg/l	23	.25	.75	0.25	.5
DBO	mg/l	> 840	132	180	111	129

TABLEAU 8

RESULTATS D'OSMOSE INVERSE POUR MELVILLE (2 juillet)

Conditions: 800 lb/po^2, 3:1 (Réservoir)

ANALYSES		RESULTATS				
TYPES	UNITES	SOLUTION CONTAMINEE	MEMBRANES (SOLUTION PURIFIEE)			
			TORAY	DSI	UOP 1001	FILMTEC
"Propriétés physiques"						
Conductivité	µS/cm	38800	6250	14860	2510	4990
Température	C	37	36	N/A	N/A	37
pH	pH	6	5.9	5.9	4.8	5.6
Alkalinité Totale	mg/l	1394	412	380	30	262
Dureté Totale	mg/l	2150	40	148	4	124
Solides dissous totaux	mg/l	27201	4120	9920	1223	3062
"Ions Majeurs"						
Calcium	mg/l	557	11	54	2	37
Magnésium	mg/l	184	3	3	1	8
Potassium	mg/l	12000	1950	4900	600	1350
Sodium	mg/l	400	73	149	16	43
Bicarbonate	mg/l	1700	503	464	37	320
Chlorure	mg/l	12100	1580	4350	570	1280
Sulphate	mg/l	260	10	10	10	24
Fer	mg/l	32.5	.1	1.2	.2	1.7
Manganèse	mg/l	6.8	.12	.42	.07	.4
"Paramètres Organiques"						
Azote Kjeldahl (N)	mg/l	275	25	52.5	32.5	30
Ammoniaque (N)	mg/l	60	15.75	34.75	20	16.5
Nitrate (NO3)	mg/l	1	1	1	1	1
Phosphate Total	mg/l	60	.5	1.25	0.25	2.75
Phosphate Ortho	mg/l	19	.25	1	0.25	1.75
DBO	mg/l	>840	147	>255	234	> 255

B. Discussion (Melville)

Les membranes que nous avons choisies pour la première partie de l'essai à Melville pourraient être divisées en deux groupes.

D'une part, nous retrouvons Toray SP110 et Filmtec FT-30 qui sont des membranes jugées très efficaces parce qu'elles ont des pores très petits. On s'attend toujours à de bonnes séparations avec ces membranes mais dépendamment du type d'eau à traiter on aura des débits de solutions purifiées relativement lents. D'un autre côté, DSI B441 et UOP 4600 sont des membranes capables, selon les cas, de bonnes séparations mais puisque leurs pores sont plus grands, les meilleurs résultats seront toujours obtenus pour des molécules d'une grandeur respectable. Il s'en suit que l'efficacité de séparation est moins élevée que disons, Toray, mais les débits d'eau purifiée seront toujours de beaucoup supérieurs. Cela représente assez bien ce qu'est l'osmose inverse en pratique. Il faut presque toujours choisir entre une membrane qui offrira une excellente séparation mais un débit lent et une autre qui sera peut-être moins efficace mais donnera d'excellents débits. Dépendamment des résultats obtenus, des contraintes économiques et des lignes de conduite environnementales, un certain type de membrane sera choisi dans le but d'effectuer un travail spécifique.

Les analyses chimiques qui ont été faites sur les solutions purifiées, concentrées et contaminées fûrent choisies dans le but d'offrir une vue d'ensemble aussi complète que possible de la performance des membranes. Au Tableau 2 nous pouvons noter que les séparations de Toray et Filmtec sont excellentes malgré le fait que nous n'opérions pas à la pression optimale de 800 lb/po^2. Techniquement parlant toutes les membranes ont fait un bon travail mais disons que les 2 premières positions vont à Toray avec des pourcentages de séparation variant de 95% à 98% pour la plupart des produits chimiques et Filmtec (90% - 96%). Des résultats semblables sont retrouvés au Tableau 3. Maintenant, comme nous l'avons dit auparavant, de bonnes séparations vont souvent de paire avec des débits de solutions purifiées plutôt lents. C'est d'ailleurs ce que nous retrouvons au Tableau 4 où les débits sont de 40 à 43 sec/L pour les membranes Toray. Nous pouvons donc dire que Toray est très efficace mais prend près de deux fois plus de temps à faire le travail que disons UOP 4600 (16-18 sec/L). Pour leur part, les membranes Filmtec semblent être la solution alternative puisqu'elles offrent de bonnes séparations et de bons débits.

De façon générale maintenant, notons que les solides dissous totaux sont séparés à environ 98% et des données excellentes sont obtenues pour les ions. Notons également que presque tous ces ions sont hydratés ce qui explique les résultats. Pour ce qui est du nitrate, la séparation est moins efficace puisque la molécule n'est pas hydratée. Dans le cas de l'ammoniaque, un étrange phénomène se produit, non seulement la séparation est faible mais il y a dans le cas des UOP 4600 concentration de l'ammoniaque dans la solution purifiée. Cet effet a déjà été observé au cours d'un essai à Shelburne (N.E.) et a été attribué à la dimension des pores.

Nous pouvons remarquer que les valeurs données au Tableau 2 pour la solution concentrée correspondent bien à la réalité puisque nous opérions à 1:1. La concentration de la solution contaminée s'est donc retrouvée 2 fois plus élevée qu'auparavant. Cependant, au Tableau 3 nous notons que les valeurs pour la solution concentrée devraient être plus élévées puisque nous étions à 3:1. Nous ne pouvons expliquer ce dernier résultat que de deux façons: soit qu'il y a eu détérioration de l'échantillon soit qu'il y a eu une mauvaise lecture lors de la prise des débits à 3:1.

Le Tableau 6 nous indique que les séparations obtenues avec Filmtec à 800 lb/po^2 sont meilleures que celles obtenues à 600 lb/po^2. Pour ce qui est de Toray, malheureusement, une fuite dû à un caoutchouc en "O" a fait en sorte que la solution purifiée fût contaminée. Il est donc impossible de juger la performance de Toray à cette nouvelle pression. Il est cependant presque certain que la séparation serait supérieure à celle obtenue auparavant. Pour ce qui est des valeurs relevées pour la solution concentrée à 1:1, elles sont consistantes.

Maintenant, si nous regardons les résultats qui se rapportent à la deuxième portion de l'essai nous avons d'intéressantes surprises. Il était anticipé que Toray et Filmtec feraient un bon travail. La seule membrane qui n'avait pas déjà été utilisée était UOP 1001. Les débits enrégistrés sont présentés au Tableau 5 alors que les résultats sont aux Tableaux 7 et 8. L'eau contaminée que nous pompions était très sale et contenait un niveau de DBO extrêmement élevé. La température de l'eau était également élevée (30 - 37°C). Les résultats obtenus représentent bien cette réalité. A haute température (30°C), les débits individuels d'eau purifiée étaient très près les uns des autres avec l'exception de DSI B441 qui était encore un peu plus rapide que les autres. Il n'en demeure pas moins qu'il n'y avait plus de différence marquée. A 3:1 nous retrouvons le même genre de relations sauf qu'il est facile de remarquer un important encrassement des membranes puisque les débits sont faibles malgré le fait que la température était alors de 37°C.

Pour ce qui est des séparations obtenues, il est surprenant de trouver des résultats de beaucoup inférieurs à ceux que nous avions obtenu lors des essais sur le marais. Cette situation est explicable par le fait que la température élevée de l'eau a causé une certaine extension des pores des membranes, laissant ainsi passer les contaminants. Les membranes DSI B441 nous offrent des résultats un peu moins bons que les autres, situation naturellement doublée d'un fort débit d'eau purifiée. Une chose est à remarquer toutefois à propos de cet essai, c'est que les UOP 1001 se sont très bien comportées avec des séparations de 93% à 99%. Il est extrapolé que si la température de l'eau n'avait pas été aussi élevée, les membranes Toray et Filmtec auraient fait un bon travail sur la solution plus concentrée de potasse qui se trouvait dans le réservoir. Une chose que l'on est certain cependant, c'est que les UOP 1001 auraient fait un bon travail à plus basse température.

Finallement, la raison pour laquelle la solution contaminée présente des concentrations plus élevées au Tableau 8 qu'au Tableau 7 est reliée au fait qu'entre les deux périodes d'échantillonnage nous avons accumulé quelques barils de solution purifiée afin de rincer nos membranes à la fin de l'essai. De cette façon nous avons réduit le volume d'eau contaminée, augmentant par le fait même la concentration dans le réservoir.

2. VILLE D'EDMONTON (EAU CONTAMINEE PAR DES INSECTICIDES/HERBICIDES)

A. Description des essais et résultats

L'essai d'Edmonton a duré 3 jours* (24, 25, 26 juin).

Le 24 juin, l'unité mobile fût configurée afin d'avoir les six cylindres à haute pression séparés en deux groupes parallèles chacun contenant six membranes en série (6 Toray SP110 et 6 Filmtec FT-30). L'essai a eu lieu à l'aéroport municipal où l'eau contaminée par des insecticides et herbicides était emmagasinée. Après avoir vérifié le niveau de chlore dans l'eau, les membranes furent conditionnées à 250 lb/po^2 pour 45 minutes, 600 lb/po^2 pour 15 minutes et 800 lb/po^2 pour 15 minutes. A 1:30 PM, la première série d'échantillons fût prélevée à 800 lb/po^2 et 1:1 de rapport de concentration. Le Tableau 9 présente tous les résultats obtenus pour Toray et Filmtec. Les analyses des échantillons furent basées sur 5 insecticides et/ou herbicides différents, représentants une grande variété de structures chimiques et de groupes fonctionnels afin de pouvoir mieux juger la susceptibilité chimique des différentes membranes testées. Nous avons gardé le rapport de concentration à 1:1 pour toute la durée de l'essai et aucun effort n'a été fait afin de concentrer plus. Aucun débit individuel n'a été enregistré. A 3:30 PM une deuxième série d'échantillons fût prélevée et ce, sous les mêmes conditions.

Au matin du 25 juin deux autres séries d'échantillons furent prélevées. Les quatres séries ensemble démontrent le comportement de Toray et Filmtec sur une période de 8 heures. Au cours de l'après-midi nous avons changé les membranes afin de tester 6 DSI B441 et 6 UOP 1001. A 3:00 PM, l'unité était en marche et les membranes conditionnées à 300 lb/po^2 pour 30 minutes, 500 lb/po^2 pour 15 minutes et 800 lb/po^2 pour 30 minutes. A 4:15 PM et 5:15 PM deux séries d'échantillons furent prélevées. Par la suite l'unité fût rincée et nettoyée comme à la fin de tous les jours.

Le 26 juin nous avons remarqué que notre ensemble de pré-filtres était encrassé et avons procédé immédiatement au changement de ces derniers. A 9:30 AM l'unité était déjà en marche et fonctionnait à 800 lb/po^2 et 1:1. Le débit combiné des solutions purifiées était alors de 7.5 sec/L. Une dernière série d'échantillons fût prélevée à 11:00 AM. Les résultats pour tous les échantillons UOP-DSI sont présentés au Tableau 10. Ce dernier essai a duré environ 6 heures.

B. Discussion (Edmonton)

Le but de cet essai étant de déterminer l'efficacité avec laquelle l'osmose inverse sépare l'eau contaminée par des insecticides et herbicides, les analyses de laboratoire ont couvert autant de types différents de composés que possible, en gardant à l'esprit que nous voulions évaluer la réponse des membranes face aux dimensions (poids moléculaires) et structures (groupes fonctionnels) des produits chimiques présents. Aucune attention particulière ne fût donnée aux débits de solutions purifiées. Les échantillons ont normalement été prélevés à intervalle de 2 heures afin de permettre une étude du comportement des membranes sur une période de 6 à 8 heures d'opération.

* Après les problèmes rencontrés à Melville avec la pompe d'alimentation, nous avons décidé d'utiliser une pompe auxilliaire. C'est avec cette deuxième pompe que nous avons fait tous les autres essais.

TABLEAU 9

RESULTATS OBTENU POUR LES MEMBRANES TORAY ET FILMTEC (Edmonton, 24 et 25 juin)

800 lb/po^2 1:1

INSECTICIDES/HERBICIDES	RESULTATS (ppm)								
NOM	SOLUTION CONTAMINEE	SOLUTION PURIFIEE*							
		TORAY				FILMTEC			
		2	4	6	8	2	4	6	8
2,4-D	67	0.007	0.03	0.029	0.038	0.03	0.024	0.033	0.2
Mecoprop	26	0.005	0.007	0.005	0.23	0.02	0.021	0.025	0.11
Acides apparentés	566	0.07	0.09	0.08	0.16	0.225	0.51	0.15	0.597
Dursban	19	ND**	ND	ND	ND	ND	ND	ND	ND
Malathion	2.6	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	3.2	ND	ND	ND	ND	ND	ND	ND	ND

* après 2, 4, 6 et 8 heures d'opération.

** ND: non détecté (Limite de détection = 1 ppb)

TABLEAU 10

RESULTATS OBTENUS POUR LES MEMBRANES UOP 1001 ET DSI B441 (Edmonton, 25 et 26 juin)

800 lb/po ^{2} 1:1

INSECTICIDES/HERBICIDES	RESULTATS (ppm)						
NOM	SOLUTION CONTAMINEE	SOLUTION PURIFIEE*					
		UOP 1001			DSI B441		
		2	4	6	2	4	6
2,4-D	299	0.3	0.3	0.043	0.6	0.023	3.7
Mecoprop	18	0.022	0.02	0.023	0.31	0.022	0.8
Acides apparentés	474	0.6	0.593	0.3	3.37	0.13	10.4
Dursban	15	0.001	ND**	ND	0.012	0.011	0.015
Malathion	3.2	0.002	ND	ND	0.012	0.015	0.024
Methoxychlor	2.0	ND	ND	ND	ND	ND	ND

* aprés 2, 4, et 6 heures d'opération.

** ND: non détecté (Limite de détection = 1 ppb)

Les résultats obtenus sont excellents. Les membranes Toray ont démontré qu'avec seulement un passage, des rejets de 99.99% pour 2,4-D, Mecoprop et acides apparentés, Dursban, Malathion et Methoxychlor sont faciles à obtenir. Pour ce qui est de Filmtec, nous obtenons approximativement le même genre de rejets (quoi que moins spectaculaires) pour les mêmes herbicides et insecticides à l'étude. Le Tableau 10 démontre la performance des deux autres membranes testées. UOP 1001 a très bien fait avec des rejets de 99.9% pour tous les composés alors que DSI B441 avec des débits d'eau purifiée beaucoup plus élevés a tout de même démontré des séparations de 99% et plus.*

Les deux séries de résultats semblent indiquer qu'aussitôt que les dimensions des molécules (poids moléculaire) atteignent une certaine valeur, l'osmose inverse se comporte plus comme une barrière physique que comme un procédé physico-chimique puisque nous avons obtenu des résultats similaires malgré de grandes différences dans les structures chimiques (annexe B). La susceptibilité chimique est donc très difficile à évaluer lorsque les dimensions moléculaires sont assez importantes.

Nous pouvons conclure que l'osmose inverse est une méthode extrêmement efficace pour séparer l'eau des insecticides et herbicides. L'application de ce procédé à l'eau contaminée résulterait en une diminution des volumes de liquides toxiques à être transportés pour fin d'enfouissement.

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* Occasionnellement un camion citerne se présentait au site afin de décharger l'eau contaminée qu'il contenait. C'est pourquoi les concentrations de notre eau contaminée sont différentes pour les essais Toray-Filmtec et UOP-DSI. Ces concentrations furent mesurées pour chaque série de solutions purifiées présentée aux Tableaux 9 et 10. Ces résultats ne sont pas publiés puisque les valeurs obtenues sont stables pour chacun des tests individuels. Le seule variation importante fût enrégistrée au moment du passage de Toray-Filmtec à DSI-UOP.

3. COMPAGNIE AYANT DES ACTIVITES EN PETROCHIMIE
(Eaux de lixivation et rejet industriel)

A. Description des essais et résultats

Les essais effectués au site pétrochimique ont eu lieu les 27, 28 et 29 juin 1985.

La première partie de ces essais fût effectuée sur le site d'enfouissement de produits chimiques où l'on retrouvait des eaux de lixiviation contaminées par des composés organiques et inorganiques. Ces eaux étaient accumulées dans un réservoir de 3000 gallons avant d'être pompées dans notre unité. Le 27 juin, l'unité mobile fût configurée afin d'avoir les six cylindres à haute pression séparés en deux groupes parallèles chacun contenant six membranes en série (6 Toray SP110 et 6 Filmtec FT-30). Vers la fin de l'avant-midi l'unité était prête à opérer et les membranes furent conditionnées à 250 lb/po^2 pour 30 minutes, 400 lb/po^2 pour 15 minutes, 600 lb/po^2 pour 15 minutes et finallement 800 lb/po^2 pour 15 minutes. Les conditions d'opération pour toute la durée de cet essai furent de 800 lb/po^2 à 2:1 de rapport de concentration. Nous n'avons pas tenté de varier ce rapport mais avons enregistré les débits d'eau purifiée à deux reprises (Tableau 11). Quatre séries d'échantillons furent prélevées: A (1:30 PM) et D (4:30 PM) qui sont des séries complètes (un échantillon de chaque port d'échantillonnage, solution contaminée et solution concentrée combinée), alors que B (2:30 PM) et C (3:30 PM) n'était que des échantillons de solutions purifiées du port #1 (Toray) et #4 (Filmtec). Les tableaux 12 (A), 13 (B, C) et 14 (D) montrent les résultats obtenus. A la fin de la journée l'unité fût rincée et nettoyée.

Le 28 juin l'unité fût transportée au deuxième site afin d'effectuer un essai à deux étapes sur une eau de rejet industriel. Ce rejet contenait parmi plusieurs produits chimiques du glycol monoéthylènique (GME) et du sodium. En premier lieu, l'unité fût configurée afin d'avoir quatre cylindres à haute pression en parallèle, chacun contenant soit 1 soit 2 membrane(s) (voir Figure 1). Pour la première fois nous avons utilisé la membrane DSI CA 4021 d'acétate de cellulose. Le but que nous poursuivions en utilisant cette première configuration, était d'étudier la solution purifiée de chacune des membranes.

TABLEAU 11

DEBITS POUR LES MEMBRANES D'OSMOSE INVERSE UTILISEES LORS DE L'ESSAI SUR LE SITE D'ENFOUISSEMENT, 27 juin (Industrie pétrochimique)

TYPE	DEBITS (sec/L)	
	3:00 PM	5:00 PM
2 x Toray soln purifiée port #1	52	55
2 x Toray soln purifiée port #2	51	46
2 x Filmtec soln purifiée port #3	30	31
2 x Filmtec soln purifiée port #4	23	25
soln purifiées combinées	3.1	3.3
soln concentrées combinées	5.8	5.3

TABLEAU 12

RESULTATS D'OSMOSE INVERSE, 27 JUIN
EAUX DE LIXIVIATION

800 lb/po^2 2:1 Série A (1:30 PM)

ANALYSES		RESULTATS					
TYPE	UNITES	SOLUTION CONTAMINEE	SOLUTION PURIFIEE MEMBRANES				SOLUTION CONCENTREE
			TORAY		FILMTEC		
			Port 1	Port 2	Port 3	Port 4	
B	mg/L	1.81	< 0.013	< 0.013	< 0.013	< 0.013	2.92
Cu	mg/L	1.71	0.210	< 0.03	< 0.03	< 0.03	3.12
Fe	mg/L	13.23	< 0.03	< 0.043	< 0.03	< 0.03	21.34
Ni	mg/L	0.44	0.06	< 0.05	< 0.05	< 0.05	0.71
Sr	mg/L	0.35	< 0.005	< 0.005	< 0.005	< 0.005	0.45
Mo	mg/L	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07
Cr	mg/L	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
Al	mg/L	0.75	< 0.15	< 0.15	< 0.15	< 0.15	0.87
K	mg/L	<100	< 100	< 100	< 100	< 100	< 100
Mg	mg/L	5.18	< 0.06	< 0.06	< 0.06	< 0.06	8.04
Ca	mg/L	35.7	2.45	1.42	0.82	0.99	56.2
Na	mg/L	8900	289	109	167	166	13900
OH^-	mg/kg	362.1	154.8	54.3	69.3	71.9	561.1
CO_3^{2-}	mg/kg	2043	64	59.6	69.9	92.3	3261
pH	unité de pH	12.1	11.7	11.3	11.4	11.5	12.2
Conductivité	µS/cm	46000	2400	1000	1000	1400	64000
COT	mg/L	1800	35.0	25	29	25.8	3000
Cl	mg/L	18000	64	39	79	43	53000
GME	mg/L	270	57	33	48	35	270
Phénoliques	µg/L	270	450	125	250	175	460
NKT	mg/L	67	-	-	-	-	69
Nitrate	mg/L	25	< 5	< 5	< 5	< 5	25
Sulphate	mg/L	464	< 5	< 5	< 5	< 5	469

TABLEAU 13

RESULTATS D'OSMOSE INVERSE, 27 JUIN
EAUX DE LIXIVIATION

800 lb/po^2 2:1 Séries B (2:30 PM) et C (3:30 PM)

ANALYSES		RESULTATS				
TYPE	UNITES	SOLUTION CONTAMINEE	SOLUTION PURIFIEE MEMBRANES			
			TORAY (port #1)		FILMTEC (port #4)	
			2:30 PM	3:30 PM	2:30 PM	3:30 PM
B	mg/L	1.81	< 0.013	< 0.013	< 0.013	< 0.013
Cu	mg/L	1.71	< 0.03	< 0.03	< 0.03	< 0.03
Fe	mg/L	13.23	< 0.03	< 0.03	< 0.03	< 0.03
Ni	mg/L	0.44	< 0.05	< 0.05	< 0.05	< 0.05
Sr	mg/L	0.35	< 0.005	< 0.005	< 0.005	< 0.005
Mo	mg/L	<0.07	< 0.07	< 0.07	< 0.07	< 0.07
Cr	mg/L	<0.015	< 0.015	< 0.015	< 0.015	< 0.015
Al	mg/L	0.75	< 0.15	< 0.15	< 0.15	< 0.15
K	mg/L	<100	< 100	< 100	< 100	< 100
Mg	mg/L	5.18	< 0.06	< 0.06	< 0.06	< 0.06
Ca	mg/L	35.7	0.92	0.76	0.49	0.52
Na	mg/L	8900	273	309	154	174
OH^-	mg/kg	362.1	161.4	162.3	85.8	91.9
CO_3^{2-}	mg/kg	204.3	58.1	74.1	58.3	52.1
pH	unité de pH	12.1	11.7	11.8	11.2	11.5
Conductivité	µS/cm	46000	2200	2100	1000	1200
COT	mg/L	1800	37	39	31	32
Cl	mg/L	18000	100	82	61	64
GME	mg/l	270	59	60	38	37
Phénoliques	µg/L	270	125	125	100	150
NKT	mg/L	67	-	-	-	-
Nitrate	mg/L	25	< 5	< 5	< 5	< 5
Sulphate	mg/L	464	< 5	< 5	< 5	< 5

TABLEAU 14

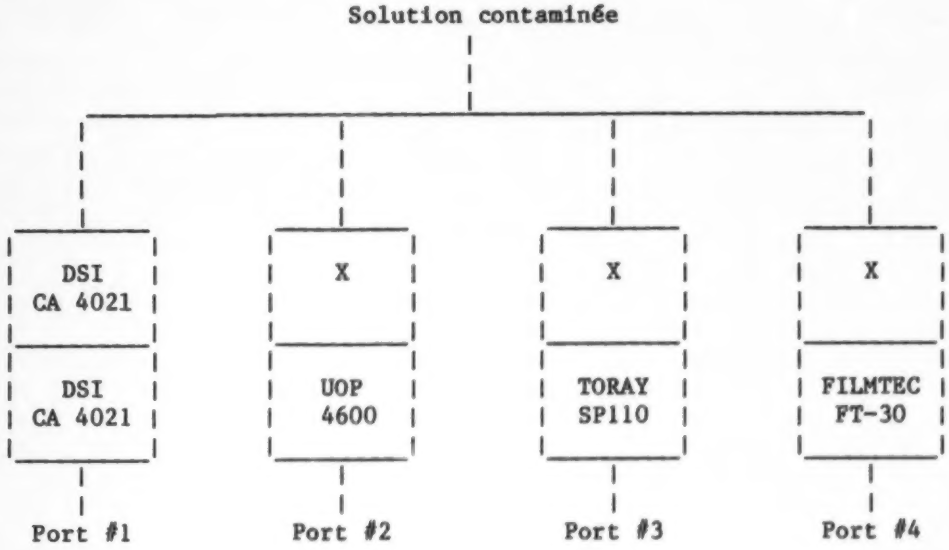
RESULTATS D'OSMOSE INVERSE, 27 JUIN
EAUX DE LIXIVIATION

800 lb/po^2 2:1 Série D (4:30 PM)

ANALYSES		RESULTATS					
TYPE	UNITES	SOLUTION CONTAMINEE	SOLUTION PURIFIEE MEMBRANES				SOLUTION CONCENTREE
			TORAY		FILMTEC		
			Port #1	Port #2	Port #3	Port #4	
B	mg/L	1.82	<0.013	<0.013	<0.013	<0.013	2.73
Cu	mg/L	1.76	<0.03	<0.03	<0.03	<0.03	2.98
Fe	mg/L	13.31	<0.03	<0.03	<0.03	<0.03	19.49
Ni	mg/L	0.46	<0.05	<0.05	<0.05	<0.05	0.67
Sr	mg/L	0.34	<0.005	<0.005	<0.005	<0.005	0.46
Mo	mg/L	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Cr	mg/L	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
Al	mg/L	0.55	<0.15	<0.15	<0.15	<0.15	0.56
K	mg/L	<100	<100	<100	<100	<100	<100
Mg	mg/L	5.18	<0.06	<0.06	<0.06	<0.06	6.12
Ca	mg/L	34.9	0.69	0.89	0.60	0.84	50.2
Na	mg/L	8800	327	139	177	198	13400
OH^-	mg/kg	363.4	175.0	71.0	80.2	94.8	551.4
CO_3^{2-}	mg/kg	1023	60.8	54.4	52.5	66.0	3115
pH	unité de pH	12.0	11.8	11.4	11.4	11.5	12.2
Conductivité	µS/cm	44000	2350	1200	1200	1300	63000
COT	mg/L	1800	39	27	30	33	2800
Cl	mg/L	18000	100	36	68	68	28000
GME	mg/L	260	63	43	41	42	350
Phénoliques	µg/L	310	75	125	200	125	430
NKT	mg/L	66	-	-	-	-	95
Nitrate	mg/L	25	< 5	< 5	< 5	< 5	25
Sulphate	mg/L	481	< 5	< 5	< 5	< 5	806

FIGURE 1

CONFIGURATION DES MEMBRANES UTILISEES LE 28 JUIN POUR LA PREMIERE PARTIE DE L'ESSAI SUR LES EAUX DE REJET INDUSTRIEL



Il était entendu que nous étions pour accumuler la solution purifiée des DSI CA 4021 dans des barils de 45 gallons dans le but de l'utiliser lors de la seconde partie de l'essai. A 1:00 PM l'unité était prête à fonctionner. Les membranes furent conditionnées à 200 lb/po^2 pour 20 minutes, 400 lb/po^2 pour 20 minutes et 600 lb/po^2 pour 20 minutes (600 lb/po^2 est la pression maximale acceptable pour DSI CA 4021). Après le conditionnement nous avons commencé à accumuler la solution purifiée des membranes d'acétate de cellulose. Les mesures des débits de solutions purifiées sont présentées au Tableau 15. Trois séries d'échantillons furent prélevées (Tableau 16). L'unité fût arrêtée vers 3:30 PM et reconfigurée pour la deuxième partie de l'essai (Figure 2).

TABLEAU 15

DEBITS DES SOLUTIONS PURIFIEES, 28 JUIN
REJET INDUSTRIEL 600 lb/po^2 1:1

PORT #	TYPE DE MEMBRANE	DEBITS (sec/L)
1	2 X DSI CA 4021	3.5
2	1 X UOP 4600	6.9
3	1 X TORAY SP110	26.4
4	1 X FILMTEC FT-30	15

TABLEAU 16

RESULTATS D'OSMOSE INVERSE POUR LA PREMIERE PARTIE DE L'ESSAI SUR LES EAUX DE REJET INDUSTRIEL, 28 JUIN 600 lb/po^2 1:1 (industrie pétrochimique)

TEMPS	SOLUTIONS	MEMBRANES (résultats en ppm)							
		DSI CA 4021		UOP 4600		TORAY SP110		FILMTEC FT-30	
		GME	SODIUM	GME	SODIUM	GME	SODIUM	GME	SODIUM
2:30 PM	CONTAMINEE	3490	74	3490	74	3490	74	3490	74
	PURIFIEE	3120	4	1970	3	936	3	1450	5
3:00 PM	CONTAMINEE	3460	74	3460	74	3460	74	3460	74
	PURIFIEE	2750	3	1880	2	841	2	1350	5
3:30 PM	CONTAMINEE	4040	75	4040	75	4040	75	4040	75
	PURIFIEE	2485	3	2785	2	727	2	1292	4

Le 29 juin nous avons effectué la deuxième partie de l'essai sur les eaux de rejet industriel. Cette partie consistait à recirculer au travers de 4 Filmtec FT-30 la solution purifiée accumulée (DSI CA 4021) et ce à 800 lb/po^2 en variant le rapport de concentration. L'essai a duré environ une heure et demi. Le fait que la température du liquide augmentait continuellement nous a empêché de poursuivre le test sur une plus longue période de temps. Les résultats obtenus sont présentés au Tableau 17. A la fin de la journée les membranes furent rincées et nettoyées.

FIGURE 2

CONFIGURATION DES MEMBRANES UTILISEES LE 29 JUIN
POUR LA SECONDE PARTIE DE L'ESSAI SUR LES EAUX DE REJET INDUSTRIEL

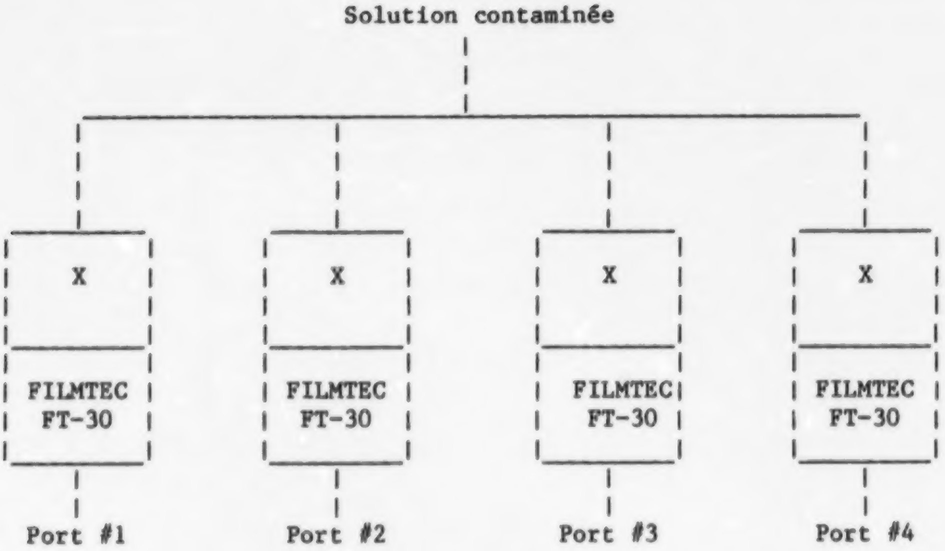

Solution contaminée
X
X
X
X
FILMTEC FT-30
FILMTEC FT-30
FILMTEC FT-30
FILMTEC FT-30
Port #1
Port #2
Port #3
Port #4

TABLEAU 17

RESULTATS D'OSMOSE INVERSE POUR LA SECONDE PARTIE
DE L'ESSAI SUR LES EAUX DE REJET INDUSTRIEL
800 lb/po^2 29 JUIN

SOLUTIONS	RAPPORTS DE CONCENTRATION					
	1:1		2:1		6:1	
	GME	Na	GME	Na	GME	Na
Purifiée	804	2	580	1	996	1
Concentrée	2507	10	3477	13	3668	14

B. Discussion (site pétrochimique)

Eaux de lixiviation

Fort de l'expérience passée (Gloucester 1984), nous savions que l'osmose inverse était capable de séparer simultanément une très grande variété de composés chimiques organiques et inorganiques. Nous anticipions donc que l'essai sur les eaux de lixiviation serait un succès. Le rapport de concentration fût conservé de façon constante à approximativement 2:1 pour des raisons purement pratiques. Aucune tentative n'a été faite pour améliorer ce rapport. Les débits présentés au Tableau 11 nous indiquent que tout demeure très stable tout au long de l'essai (pas de dépôt sur les membranes). Les membranes Filmtec ont encore une fois démontrées qu'elles pouvaient travailler plus rapidement que les Toray mais comme nous le montre les résultats présentés aux Tableaux 12, 13 et 14, cette rapidité relative ne va pas de pair avec des pourcentages de séparation inférieurs.

Si nous étudions les résultats en nous déplacant de haut en bas le long des tableaux, nous remarquons le comportement suivant: nous avons obtenu des rejets de 99.9% pour tous les métaux et ce avec chacune des membranes ce qui signifie que ces dernières furent très stables tout au long de l'essai. Pour ce qui est du sodium nous n'avons que des rejets de 96% à 98%. Ces valeurs sont inférieures à ce que nous nous attendions. Nous attribuons cette situation à la présence de toutes sortes de métaux à de telles concentrations que les membranes furent probablement surchargées. Le calcium est stable à 98% de même que les carbonates (97%). Les ions hydroxides pour leur part se comportent bizarrement en présentant des rejets de 50% à 80% avec Toray et près de 75% avec Filmtec. Etant donné que l'on a affaire à une petite molécule, même si elle est hydratée, il était anticipé que son rejet serait faible. Le pH est demeuré relativement stable autour de 11.5 mais nous remarquons que la solution purifiée est moins basique que la solution contaminée. Cette situation est probablement liée au rejet de plusieurs espèces inorganiques. La "conductivité" et le "COT" furent rejetés à près de 98%. D'excellents résultats furent obtenus pour les chlorures (99.5%).

Le GME semble être mieux séparé par Filmtec (86%) que par Toray (77%). Pour ce qui est des composés phénoliques nous obtenons des résultats surprenants pour Toray (76%-54%) et Filmtec (63%-52%). En Colombie-Britannique (1984), l'osmose inverse avait réussi à rejeter 99.9% des chlorophénols présents à une concentration de 2000 ppm. Il était donc anticipé que les résultats seraient similaires. Il semble que la présence de "Cl" sur les anneaux phénoliques soit déterminante pour obtenir de bonnes séparations. Finallement, les nitrates, sulphates et NKT présentent comme prévu des rejets de 99%. Les valeurs pour les solutions concentrées sont en accord avec les valeurs correspondantes de solutions contaminées compte tenu du rapport de concentration utilisé au cours de l'essai.

En conclusion nous pouvons dire que, générallement, Filmtec a présenté de meilleurs débits d'eau purifiée et des résultats légèrement supérieurs à Toray. Les deux types de membranes présentent des résultats exceptionnels.

Eaux de rejet industriel

Cette deuxième partie de l'essai a dû être effectuée en deux étapes étant donné les produits chimiques présents. Les eaux de rejet contenaient en plus d'une grande variété de composés organiques et inorganiques, du glycol monoéthylènique (GME) et du sodium. Il s'agissait de trouver un moyen pour concentrer le rejet afin de mieux disposer du GME et ce en absence de sodium.

i) Première étape

La Figure 1 présente la configuration utilisée lors de cette première étape. Comme nous pouvons voir deux membranes DSI CA 4021 furent utilisées. Elles furent choisies parce qu'elles possèdent le pouvoir de séparer le sodium des molécules organiques. La solution purifiée obtenue de ces membranes était accumulée dans des barils adjacents (cette solution contenait surtout des molécules organiques et seulement une infime quantité de composés inorganiques). Les membranes UOP 4600 furent choisies dans un but expérimental parce que l'on croyait que leur comportement serait proche des DSI CA 4021. Enfin, Toray et Filmtec furent utilisées afin d'évaluer leur pouvoir de séparation. Les résultats présentés au Tableau 16 confirment les comportements des membranes. Si l'on considère comme stable les concentrations en GME et Na présentes dans la solution contaminée (3500-4000 ppm GME, 74 ppm Na), nous remarquons que dans le cas de DSI CA 4021 nous récupérons entre 60% et 90% du GME alors que 96% du sodium est rejeté; ce qui signifie que vraiment les membranes composées d'acétate de cellulose rejettent les "inorganiques" et laissent passer les petites molécules organiques. Si nous portons en graphique la concentration du GME dans la solution purifiée en fonction du temps, nous retrouvons une pente négative. Cela signifie que le conditionnement des membranes n'avait probablement pas été assez long. Normalement la concentration en GME aurait dû être constante. Toutefois, une bonne extrapolation nous indiquerait probablement une récupération de 50% à 70% du GME et ce avec un seul passage.

La membrane UOP 4600 pour sa part s'est comportée presque comme les "acétate de cellulose". En fait, les résultats démontrent un rejet de 97% du sodium et une récupération de 55% à 70% du GME. Ici aussi nous pouvons remarquer une certaine instabilitée de la concentration du GME dans la solution purifiée. En plus, le Tableau 15 nous indique que les débits de solution purifiée des membranes UOP 4600 sont presque semblables à ceux des DSI CA 4021 ce qui renforce l'idée de similarité dans les comportements.

Les Toray SP110 présentent des rejets de 97% pour le sodium et de 70% à 80% pour le GME ce qui est excellent si l'on considère la grosseur de la molécule (comparable aux résultats obtenus sur les eaux de lixiviation). Cette bonne séparation naturellement est doublée par un faible débit d'eau purifiée (26 sec/L). Pour ce qui est des Filmtec FT-30 nous retrouvons un rejet de sodium de 95% alors que le GME pour sa part est rejeté de 60% à 70%, ce qui est moins que ce que nous anticipions étant donné les réjets de plus de 80% obtenus lors des essais au site d'enfouissement.

En résumé, nous pouvons dire que toutes les membranes ont eu de bons rejets de sodium mais elles se sont toutes comportées différemment par rapport au GME.

ii) Deuxième étape

La Figure 2 présente la configuration utilisée lors de cette deuxième étape. Nous n'avons utilisé que des Filmtec FT-30. Le but de cette étape était d'étudier jusqu'à quel point l'on pouvait concentrer le GME accumulé dans les barils (Tableau 17). Il est interprété, à partir des résultats obtenus pour les solutions purifiées et concentrées, que la concentration en GME présente dans la solution contaminée était inférieure à celle enregistrée le jour précédent (approximativement 1500 ppm au lieu de 2400 ppm). Cette situation est probablement le fruit d'une dilution occasionnée par la présence d'eau résiduelle dans l'unité. Les résultats obtenus démontrent que nous avons concentré autant le GME que le sodium. Toutefois, nous avons obtenu une solution finale contenant plus de deux fois la concentration initiale de GME mais seulement 13 ppm de sodium. Notons également que le Tableau 17 semble indiquer que la qualité de la solution concentrée varie avec le rapport de concentration. Les conditions optimales étant 800 lb/po^2 et 2:1.

Conclusions:

Melville:

- L'osmose inverse est un bon moyen de traiter l'eau de lavage de wagons contenant de la potasse;
- Avec des rejets de près de 99%, Toray SP110, Filmtec FT-30 et UOP 1001 semblent être excellentes pour nettoyer l'eau de potasse; et
- Les hautes températures (30-37°C) influencent non seulement les débits d'eau purifiée mais aussi la qualité de cette eau et ce pour la plupart des membranes sauf UOP 1001.

Edmonton:

- L'osmose inverse peut être utilisée pour nettoyer de l'eau contaminée par des insecticides et/ou herbicides; et
- Les membranes Toray SP110, Filmtec FT-30, UOP 1001 et DSI B441 semblent être excellentes pour nettoyer des déchets toxiques liquides.

Compagnie (Pétrochimie):

- La présence de "Cl" sur les composés phénoliques apparaît être essentielle si l'on désire obtenir des rejets de l'ordre de 99%;
- L'osmose inverse s'est encore une fois avérée efficace sur les eaux de lixiviation; et
- Un essai d'osmose inverse à deux étapes a prouvé qu'il est possible de séparer des composés organiques et inorganiques et de les concentrer individuellement.

Remerciements

Nous voudrions exprimer notre gratitude au Canadien National, à la Région de l'Ouest et du Nord du SPE ainsi qu'à la compagnie ayant des activités en pétrochimie pour leur participation financière au projet.

De plus, nous remercions "Clifton Associates" et "Alberta Environment" pour les analyses qu'ils ont effectuées sur nos échantillons.

Références

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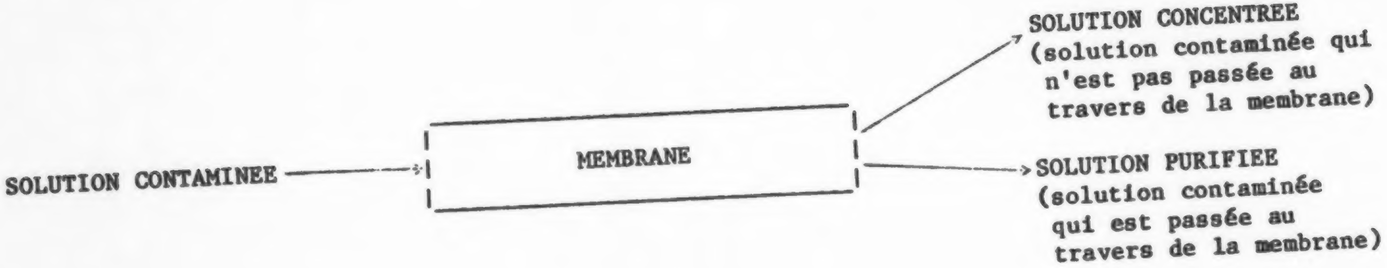
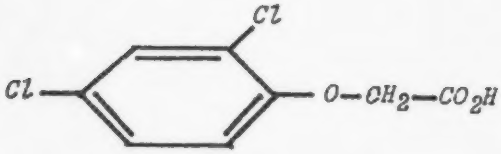
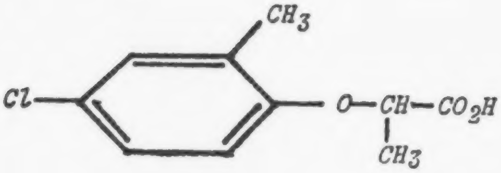
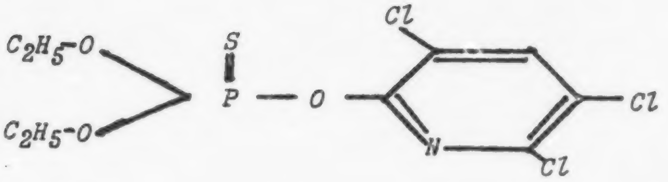
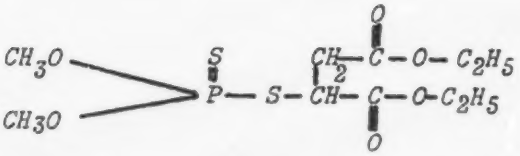
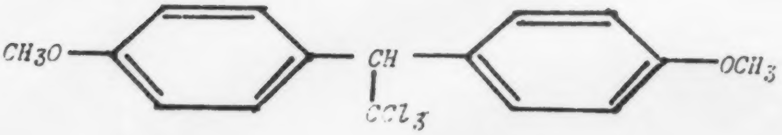
- Reverse Osmosis for Cleanup of Spilled Wood Protection Solution, J.B. Straforelli, H. Whittaker. Environment Canada 1985.
- Concentration of Dilute Chemical Landfill Leachate by Reverse Osmosis, H. Whittaker, Environment Canada, C. Adams, Waterloo University 1985.

P.S. This publication is also available in English.

ANNEXE A


SOLUTION CONTAMINEE
MEMBRANE
SOLUTION CONCENTREE
(solution contaminée qui n'est pas passée au travers de la membrane)
SOLUTION PURIFIEE
(solution contaminée qui est passée au travers de la membrane)

ANNEXE B

Nom	Structure chimique
2,4-D	
Mecoprop	
Dursban	
Malathion	
Methoxychlor	

MEMBRANE TECHNOLOGY APPLICATIONS IN WESTERN CANADA

Jean Tremblay
Project Scientist
Environment Canada
Environmental Protection Service
Environmental Emergencies Technology Division

INTRODUCTION

The Environmental Emergencies Technology Division (EETD) of the Environmental Protection Service (EPS) was requested by Canadian National Railways, the Western and Northern Region of EPS and a petrochemical company to bring the mobile reverse osmosis (RO) unit to Western Canada for demonstrations/trials. The objectives were to determine and/or demonstrate the applicability of reverse osmosis technology to the following contaminated waters:

- potash cars wash water (CN)
- insecticides and herbicides (EPS)
- chemical landfill leachate (Petrochemical Co.)
- industrial process waste water stream (Petrochemical Co.)

The trials were carried out in the summer of 1985.

BACKGROUND

- The Canadian National Railway has an important hopper car wash facility in Melville (Saskatchewan). The contaminated wash water from the site ends up in an evaporation pond. Analysis shows high total dissolved solids (TDS), a number of anions and cations (especially potassium and chloride), ammonia, nitrate and a high BOD level. The pond occasionally overflows and contaminates the environment. Aware of the problem, CN requested our help in determining the applicability of RO to their water.

- Alberta uses large quantities of insecticides and herbicides on its territory. Many farmers buy drums of the chemicals to spray on their land. Some cities like Edmonton rinse the drums once they have been emptied to make sure that there is no trace of the chemicals left. That "rinse" usually is stored in underground tanks and disposed of in chemical landfills. The cost involved in shipping the contaminated water is very high, and there are environmental risks. The Western and Northern region of EPS who were concerned with the problem, came up with RO as a possible solution. A trial was arranged to test our unit against insecticide/herbicide contaminated water.

- A petrochemical company that wishes to remain anonymous experienced some problems in two specific areas over the years.

First, the company has a chemical landfill on the plant site. The leachate from that landfill is being accumulated and then disposed of. It contains a wide variety of organic and inorganic contaminants. Knowing that RO already performed well at the Gloucester Landfill in 1984 it was suggested as a possible solution at this site.

Secondly, a waste water industrial process stream that was injected directly into the environment contained among other organic and inorganic molecules, monoethylene glycol and sodium. A trial was set up to see if RO could separate these compounds and concentrate the glycol thus minimizing the environmental impact.

1. CANADIAN NATIONAL RAILWAY COMPANY (Melville Sask.)

A. Procedures and Results

The trial in Melville lasted 4 days (June 18, 19, 20 and July 2, 1985).

On June 18 the RO mobile unit was configured with four parallel banks of two membrane elements in series (see Table 1). The unit was set up near the evaporation pond where the wash water ends up. The membranes were conditioned at 200 PSI for 1 hour, 400 PSI for 15 minutes and 600 PSI for about 1 hour. Minor feed pump problems were experienced that day. Everything was ready to start the trial the next morning.

TABLE 1

RO MEMBRANES USED IN MELVILLE SASK. ON JUNE 18 AND 19/85

PORT #	TYPE*	MAX. PRESSURE (PSI)	STRUCTURE
1	TORAY SP110	800	polyether-polysulphone
2	DSI B441**	800	polyamide-polysulphone
3	UOP 4600***	600	polyether/polyamide-polysulphone
4	FILMTEC FT-30	800	polyamide-polysulphone

* All the membranes were spiral wound, thin film composites.
** DSI = Desalination Inc.
*** UOP = United Oil Product

On June 19, the unit was started at 8:00 AM and run at 600 PSI and 1:1 concentration ratio. At 9:00 AM we took our first set of samples. The results are shown in Table 2. After a couple of hours we experienced some feed pump problems again. The unit was shut down for about 3 hours and the pump repaired. By 2:30 PM the unit was started and operated at 600 PSI and 3:1 for half an hour before a second set of samples was taken (Table 3). The flow rate measured during the day are presented in Table 4.

On June 20, we continued the test on the "pond" water. The unit was reconfigured in two parallel banks of 6 membrane elements each (6 Toray SP110 and 6 Filmtec FT-30). The purpose of that test was to determine what type of flow rates the new configuration would give us and to evaluate the quality of the permeate obtained at 800 PSI from the 2 anticipated "best" membranes. The elements were conditioned at 400 PSI for 30 minutes, 600 PSI for 15 minutes and 800 PSI for 15 minutes. The first set of samples was taken when the combined permeate flow rates was 20 L/minute at 800 PSI, 1:1 concentration ratio.

TABLE 2

RO RESULTS FROM MELVILLE (SASK.) JUNE 19

Conditions: 600 PSI, 1:1 (Pond)

ANALYSES		RESULTS					
			MEMBRANES (PERMEATE)				CONCENTRATE
TYPE	UNITS	FEED	TORAY	DSI	UOP 4600	FILMTEC	
"Physical Properties"							
Conductivity	µS/cm	18400	506	2922	3464	724	+50000
Field Temperature	C	20	28	22	21.9	21.5	30
pH	pH Units	8.3	10	9.1	8.4	9.6	8.5
Total Alkalinity	mg/1	653	80	69	50	50	738
Total Hardness	mg/1	2790	4	60	8	4	5760
Total Dissolved Solids	mg/1	18914	254	2170	2320	505	59696
"Major Ions"							
Calcium	mg/1	380	2	10	2	2	728
Magnesium	mg/1	447	1	9	1	1	957
Potassium	mg/1	5600	85	730	960	195	12600
Sodium	mg/1	1600	27	215	187	48	3525
Bicarbonate	mg/1	797	0	35	51	0	791
Chloride	mg/1	8300	88	1090	1300	224	18600
Sulphate	mg/1	1640	10	32	10	10	3600
Iron	mg/1	1	0.1	0.1	0.1	0.1	1.6
Manganese	mg/1	.59	.06	.05	.04	.04	.73
"Organic Parameters"							
Kjeldahl Nitrogen as N	mg/1	110	12.5	22.5	1.8	12.5	140
Ammonia as N	mg/1	16.5	10	14	22.5	8.25	33.5
Nitrate as NO3	mg/1	90	8	25	14	10	140
Total Phosphate	mg/1	5.5	.25	.5	.25	.25	7.25
Ortho Phosphate	mg/1	3	.01	.02	.01	.02	1.25
BOD	mg/1	49	1	1	1	1	98

TABLE 3

RO RESULTS FROM MELVILLE (SASK.) JUNE 19

Conditions: 600 PSI, 3:1 (Pond)

ANALYSES		RESULTS					
TYPE	UNITS	FEED	MEMBRANES (PERMEATE)				CONCENTRATE
			TORAY	DSI	UOP 4600	FILMTEC	
"Physical Properties"							
Conductivity	μS/cm	18400	677	24860	4400	1858	N/A
Field Temperature	C	20	29.5	35	29	31.2	31
pH	pH Units	8.3	10.1	9	8.8	9.4	8.5
Total Alkalinity	mg/l	653	88	163	57	68	763
Total Hardness	mg/l	2790	4	304	16	4	6120
Total Dissolved Solids	mg/l	18914	304	11998	3235	1325	45322
"Major Ions"							
Calcium	mg/l	380	2	66	5	2	792
Magnesium	mg/l	447	1	34	1	1	1006
Potassium	mg/l	5600	110	4200	1280	420	14600
Sodium	mg/l	1600	33	1250	274	137	3850
Bicarbonate	mg/l	797	0	89	28	7	797
Chloride	mg/l	8300	122	6100	1610	700	20000
Sulphate	mg/l	1640	10	114	10	10	4080
Iron	mg/l	1	0.1	0.1	0.1	0.1	1.2
Manganese	mg/l	.59	.04	.1	.05	.04	.74
"Organic Parameters"							
Kjeldahl Nitrogen as N	mg/l	110	20	40	45	20	175
Ammonia as N	mg/l	16.5	11.25	32.5	34	15	74
Nitrate as NO3	mg/l	90	5	90	17	23	130
Total Phosphate	mg/l	5.5	.5	.25	.5	.25	7.5
Ortho Phosphate	mg/l	3	.01	.03	.01	.01	1.5
BOD	mg/l	49	1	1	1	1	95

The results are presented in Table 6. The samples were taken from port #2 and #3 which represent the dirtiest permeate to be expected (it was found out later that a used "O" ring caused some concentrate to leak into the permeate of the Toray membranes, giving results which are not as good as expected). The flow rates stayed stable for more than an hour (20 L/min). We then went up to 4:1 of concentration ratio and noticed the flow rates dropping to 15 L/minute because of membrane plugging. We decided to end this portion of the trial and moved to an area where there was more concentrated potash wash water. Unfortunately, because of the pump problems mentioned earlier and schedule restraint, we had to postpone the second test until July 2nd.

TABLE 4

RO MEMBRANES PERMEATE FLOW RATES: JUNE 19 (Melville)

PORT #	MEMBRANE TYPE	FLOW RATES (sec/L)	
		1:1	3:1
1	2 X TORAY SP 110	40	43
2	2 X DSI B441	20	18
3	2 X UOP 4600	16	18
4	2 X FILMTEC FT-30	26	27

On July 02, we were back in Melville. The unit was configured with four parallel banks of 2 membrane elements in series as in Table 1 except that instead of using the UOP 4600, we used UOP 1001 membranes capable of handling 800 PSI of pressure. During our absence, CN had accumulated 500 gallons of concentrated wash water. It was understood that we were going to recirculate that 500 gallons through our unit for most of the trial in order to have enough water to last two hours. The temperature of the water being 29°C at the beginning, we kept the pretreatment to a minimum (30 minutes) so that the water temperature would not increase too much because of the recirculation. The flow rates recorded during the trial are listed in Table 5. We can see that at 3:1 some plugging occurred. The first set of samples was taken at 800 PSI 1:1 and the second, half an hour later at 800 PSI at 3:1. The results are shown in Table 7 and 8. The feed temperature at the end of the trial was 37°C.

TABLE 5

RO MEMBRANES PERMEATE FLOW RATES: JULY 02 (Melville)

PORT #	MEMBRANE TYPE	FLOW RATES (sec/L)	
		1:1 (30°)	3:1 (37°)
1	2 X TORAY SP 110	19	40
2	2 X DSI B441	13	23
3	2 X UOP 1001	19	41
4	2 X FILMTEC FT-30	16	40

TABLE 6

RO RESULTS FROM MELVILLE (SASK.) JUNE 20

Conditions: 800 PSI, 1:1 (Pond)

ANALYSES		RESULTS			
TYPE	UNITS	FEED	MEMBRANES (PERMEATE)		CONCENTRATE
			TORAY*	FILMTEC	
"Physical Properties"					
Conductivity	µS/cm	2658	3229	356	+50000
Field Temperature	C	21.2	22	22.5	24
pH	pH Units	8.6	8.8	9.9	8.3
Total Alkalinity	mg/1	402	58	50	706
Total Hardness	mg/1	3280	64	4	6320
Total Dissolved Solids	mg/1	25106	2495	279	50121
"Major Ions"					
Calcium	mg/1	422	16	2	832
Magnesium	mg/1	540	6	1	1030
Potassium	mg/1	8400	860	96	16000
Sodium	mg/1	2140	278	27	4175
Bicarbonate	mg/1	388	39	0	861
Chloride	mg/1	11200	1250	126	23000
Sulphate	mg/1	1950	14	10	4200
Iron	mg/1	1	.4	.1	1.5
Manganese	mg/1	.35	.04	.04	.73
"Organic Parameters"					
Kjeldahl Nitrogen as N	mg/1	87.5	2	20	150
Ammonia as N	mg/1	43.5	8.5	6.75	79.5
Nitrate as NO3	mg/1	66	16	3	98
Total Phosphate	mg/1	5.25	.75	.5	9
Ortho Phosphate	mg/1	1.5	0.25	.025	2
BOD	mg/1	78	2	2	70

* Leak due to lose "O" ring.

TABLE 7

RO RESULTS FROM MELVILLE (SASK.) JULY 02

Conditions: 800 PSI, 1:1 (Tank)

ANALYSES		RESULTS				
TYPE	UNITS	FEED	MEMBRANES (PERMEATE)			
			TORAY	DSI	UOP 1001	FILMTEC
"Physical Properties"						
Conductivity	µS/cm	36800	2000	5640	670	1460
Field Temperature	C	N/A	30	32	32	32
pH	pH Units	6.2	5.8	6	4.5	5.9
Total Alkalinity	mg/l	1230	170	160	0	100
Total Hardness	mg/l	1880	4	44	4	44
Total Dissolved Solids	mg/l	25709	1257	3628	322	870
"Major Ions"						
Calcium	mg/l	512	2	10	2	13
Magnesium	mg/l	146	1	5	1	3
Potassium	mg/l	11600	570	1700	158	410
Sodium	mg/l	360	24	58	4	14
Bicarbonate	mg/l	1501	207	195	0	122
Chloride	mg/l	11300	456	1660	170	348
Sulphate	mg/l	290	10	10	10	10
Iron	mg/l	17	.1	.5	.1	.6
Manganese	mg/l	6.1	.06	.28	.26	.13
"Organic Parameters"						
Kjeldahl Nitrogen as N	mg/l	237.5	17.5	20	15	15
Ammonia as N	mg/l	32.5	4.75	12.25	6.25	4.75
Nitrate as NO3	mg/l	1	1	1	1	1
Total Phosphate	mg/l	50	0.25	.25	0.25	1
Ortho Phosphate	mg/l	23	.25	.75	0.25	.5
BOD	mg/l	>840	132	180	111	129

TABLE 8

RO RESULTS FROM MELVILLE (SASK.) JULY 02

Conditions: 800 PSI, 3:1 (Tank)

ANALYSES		RESULTS				
TYPE	UNITS	FEED	MEMBRANES (PERMEATE)			
			TORAY	DSI	UOP 1001	FILMTEC
"Physical Properties"						
Conductivity	µS/cm	38800	6250	14860	2510	4990
Field Temperature	C	37	36	N/A	N/A	37
pH	pH Units	6	5.9	5.9	4.8	5.6
Total Alkalinity	mg/1	1394	412	380	30	262
Total Hardness	mg/1	2150	40	148	4	124
Total Dissolved Solids	mg/1	27201	4120	9920	1223	3062
"Major Ions"						
Calcium	mg/1	557	11	54	2	37
Magnesium	mg/1	184	3	3	1	8
Potassium	mg/1	12000	1950	4900	600	1350
Sodium	mg/1	400	73	149	16	43
Bicarbonate	mg/1	1700	503	464	37	320
Chloride	mg/1	12100	1580	4350	570	1280
Sulphate	mg/1	260	10	10	10	24
Iron	mg/1	32.5	.1	1.2	.2	1.7
Manganese	mg/1	6.8	.12	.42	.07	.4
"Organic Parameters"						
Kjeldahl Nitrogen as N	mg/1	275	25	52.5	32.5	30
Ammonia as N	mg/1	60	15.75	34.75	20	16.5
Nitrate as NO3	mg/1	1	1	1	1	1
Total Phosphate	mg/1	60	.5	1.25	0.25	2.75
Ortho Phosphate	mg/1	19	.25	1	0.25	1.75
BOD	mg/1	>840	147	>255	234	>255

B. Discussion (Melville)

The membranes selected for the first portion of the trial, can be classified into two groups.

Toray SP110 and Filmtec FT-30 are efficient membranes because they are very tight. Good rejections are always expected but depending on the type of water pumped through them, relatively slow flow rates are obtained. DSI B441 and UOP 4600 are, on the other hand, membranes that can be very efficient depending on the type of contaminants but they are not as tight as the Toray-Filmtec group. Good rejections might be obtained but the flow rates will always be very good. That is a good representation of what RO is all about, you almost always have to choose between a highly efficient membrane with low flow rates and a less efficient (but still very good) membrane with high flow rates. Depending on the results obtained, economics and environmental guidelines, the proper type of membrane for a specific application is selected.

The chemical analysis performed on the membrane's permeates, concentrates and feed have been especially choosen to give as wide a view as possible to the membrane performance. In Table 2, we can see that even if most membranes were not operating at the 800 PSI optimum pressure, the rejections were very good, especially those of Toray and Filmtec. Technically speaking, all the membranes did a good job but Toray's rejections varied from 95% to 98% for most of the chemicals and Filmtec's varied from 90% to 96% (giving them first two places). The same type of results are obtained when we look at Table 3. Now the fact that Toray had excellent rejections is not without paying the price. Indeed, Table 4 shows flow rates of 40-43 sec/L for that type of membrane. It might be more efficient as far as removal is concerned, but it takes more than twice the time than lets say UOP 4600 (16-18 sec/L). Filmtec seems to be a good alternative with good rejection and a good flow rate. The total dissolved solids rejection is in the 98% range and excellent data are obtained for anions and cations. Almost all of those ions are hydrated which explains the good rejections. As far as nitrate is concerned the rejection goes down because it is a small molecule that is not hydrated. In the case of ammonia a strange phenomenon occurred. Not only the rejection is not good (too small) but in the case of the UOP 4600 there is actually concentration of ammonia in the permeate. That effect has been observed before during a trial in Shelburne (N.S.) and is known to be related to pore size.

We can notice that the concentrate value in Table 2 is about what it should be since at 1:1 the feed is concentrated by a factor near 2. In Table 3 though, the concentrate should be a lot higher in concentration than what it is. The only explanation for that strange result is either sample deterioration or a bad reading as far as the 3:1 ratio is concerned.

The results shown in Table 6 indicate that the Filmtec rejections were better at 800 PSI (optimum pressure). As far as the Toray results are concerned, unfortunately, a leak due to an old "O" ring contaminated the permeate. It is therefore impossible to judge the performance at that new pressure. A good guess would be that the rejections would have been at least equivalent to the one obtained at 600 PSI. The concentrate values are consistent for 1:1.

As far as the last portion of the trial (tank) is concerned, the results are very surprising. It was anticipated that once again Toray and Filmtec would have done a good job. The only new membrane tested at that point was the UOP 1001. The results are presented in Table 5 for the flow rates and Table 7 and 8 for the rejections. The feed water was very dirty and contained extremely high BOD's. The temperature of the water was very high (30-37°C). The results obtained reflect this fact. At high temperature (30°C), the flow rates of the membranes were very close to each other with the exception of the DSI B441 that were still faster than the others. At 3:1 we have the same relations except that we notice an important plugging, flow rates are slow even if the temperature is higher (37°C).

As far as rejection is concerned, surprisingly Toray and Filmtec were far from being as good as they were on the pond water. That is probably due to the high temperature causing extension of the membrane pores allowing contaminants to go through. DSI's results follow the same pattern except that they are even worse than the others. Surprisingly the UOP 1001 shows very good rejections (93-99%). It is extrapolated that Toray and Filmtec normally would have done as good a job on the more concentrated potash water treated in the tank if it was not for the temperature influence. We know that UOP 1001 would have been very good at low temperature.

Finally, the reason why the feed water is more concentrated in Table 8 than in Table 7 is because in between sampling we accumulated some permeate with which to flush the membranes at the end of the trial. That way, we reduced the volume of contaminated water, automatically increasing the concentration.

2. CITY OF EDMONTON INSECTICIDE/HERBICIDE CONTAMINATED WATER

A. Procedures and Results

The trial in Edmonton lasted 3 days *(June 24, 25 and 26, 1985).

On June 24 the unit was configured with two parallel banks of 6 membrane elements in series. (6 Toray SP110 and 6 Filmtec FT-30). The trial took place at the municipal airport where some of the pesticide wash water was stored. After having checked for the free chlorine content of the water, the membranes were conditioned at 250 PSI for 45 minutes, 600 PSI for 15 minutes and 800 PSI for 15 minutes. At 1:30 PM the first set of samples was taken under the 800 PSI 1:1 conditions. Table 9 presents all the results obtained for Toray and Filmtec. The analysis of the samples were based on 5 different insecticides and/or herbicides that represent a wide variety of chemical structures and functional groups. This variety enables us to judge the chemical susceptability of the membrane tested. We kept a 1:1 concentration ratio for the entire trial and there were no attempt to concentrate more. No flow rates were recorded. At 3:30 PM a second set of samples was taken under the same conditions.

* After the problems encountered with the feed pump in Melville, we decided to bypass it and use an auxillary one. It is with that second pump that the rest of the trial was done.

TABLE 9

EDMONTON'S TORAY AND FILMTEC SERIES OF RESULTS - JUNE 24 AND 25

800 PSI 1:1

INSECTICIDE/HERBICIDE	RESULTS (ppm)								
NAME	FEED	PERMEATES*							
		TORAY				FILMTEC			
		2	4	6	8	2	4	6	8
2,4-D	67	0.007	0.03	0.029	0.038	0.03	0.24	0.033	0.2
Mecoprop	26	0.005	0.007	0.005	0.23	0.02	0.021	0.025	0.11
Related Acids	566	0.07	0.09	0.08	0.16	0.225	0.51	0.15	0.597
Dursban	19	ND**	ND	ND	ND	ND	ND	ND	ND
Malathion	2.6	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	3.2	ND	ND	ND	ND	ND	ND	ND	ND

* After 2, 4, 6 and 8 hours of operation.

** ND: not detectable (detection limit = 1 ppb)

On the morning of June 25 two other sets of samples were taken. The four sets together show the behaviour of the Toray and Filmtec membranes over a period of 8 hours. In the afternoon we changed the membranes and put in 6 DSI B441 and 6 UOP 1001. By 3:00 PM the unit was running and the membranes were conditioned at 300 PSI for 30 minutes, 500 PSI for 15 minutes and 800 PSI for 30 minutes. At 4:15 PM and 5:15 PM two sets of samples were taken. The unit was then shut down and as at the end of every day, rinsed and cleaned.

On June 26 we noticed that our prefilters were dirty. We put in a new set of 25 μm polyester cartridge filters. By 9:30 AM the unit was running again at 800 PSI 1:1. The combined permeate flow rate at the time was 7.5 sec/L. A last set of samples was taken at 11:00 AM. The results for all the UOP-DSI samples are presented in Table 10. The UOP-DSI trial lasted about 6 hours.

B. Discussion (Edmonton)

The purpose of the trial being to determine how well RO works on insecticide/herbicide contaminated water, the laboratory analyses covered as many different types of each as possible. The objective was to evaluate the membranes response to the size (molecular weight) and the structure (functional group) of the chemicals present in the original solution. No emphasis was put on flow rates. The samples were usually taken at 2 hour intervals giving us the chance to study the membranes behaviour over 6 to 8 hours of operations. The results obtained are excellent. Toray shows that, with only one pass, removals of 99.99% for 2,4-D, Mecoprop and related acids, Dursban, Malathion and Methoxychlor are easy to attain. As far as Filmtec is concerned, we obtained approximately the same type of removals (although less spectacular) for the same compounds studied. Table 10 shows the performance of the other two membranes tested. UOP 1001 did very well with rejections of 99.99% for all the chemicals and so did DSI B441 with removals of 99% or more.*

The two sets of results tend to indicate that as soon as we reach a certain molecular size (molecular weight), the reverse osmosis process behaves more like a physical barrier than as a physico-chemical one since we obtained similar results for a wide variety of chemical structures (Annex A). The chemical susceptibility is difficult to evaluate when the molecular size is too large.

We can conclude that reverse osmosis is a highly efficient method to separate insecticides/herbicides and water. The application of that process to contaminated water would result in reduced volume of toxic liquids to be transported to secure landfill or alternative.

* Occasionally, tank trucks filled with contaminated water came to the site to pump their waste into our feed solution. That is why the concentration of the "feed" is not the same for the Toray-Filmtec test and the UOP-DSI one. Concentrations were monitored for each set of permeate samples presented in Table 9 and 10. Those results are not reported since the concentrations were pretty stable over each individual test. The only important variation happened during the change over from Toray-Filmtec to UOP-DSI.

TABLE 10

EDMONTON'S UOP AND DSI SERIES OF RESULTS - JUNE 25 AND 26

800 PSI 1:1

INSECTICIDE/HERBICIDE	RESULTS (ppm)						
NAME	FEED	PERMEATES*					
		UOP 1001			DSI B441		
		2	4	6	2	4	6
2,4-D	299	0.3	0.3	0.043	0.6	0.032	3.7
Mecoprop	18	0.022	0.020	0.023	0.31	0.022	0.8
Related Acids	474	0.600	0.593	0.3	3.37	0.13	10.4
Dursban	15	0.001	ND**	0.001	0.012	0.011	0.015
Malathion	3.2	0.002	ND	ND	0.012	0.015	0.024
Methoxychlor	2.0	ND	ND	ND	ND	ND	ND

* After 2, 4, and 6 hours of operation.
** ND: not detectable (detection limit = 1 ppb)

3. PETROCHEMICAL CO. (Landfill Leachate and Industrial Process Waste Stream)

A. Procedure and Results

The trials at the Petrochemical Co. took place June 27, 28 and 29, 1985.

On June 27 the unit was configured with two parallel banks of 6 membranes elements in series (6 Toray SP110 and 6 Filmtec FT-30). The first portion of that trial was performed on a landfill leachate that contained both organic and inorganic contaminants. The leachate was collected in a 3000 gallon tank from which we were feeding. By noon the unit was ready and we conditioned the membranes at 250 PSI for 30 minutes, 400 PSI for 15 minutes, 600 PSI for 15 minutes and finally 800 PSI for 15 minutes. The conditions throughout that portion of the trial were 800 PSI at about 2:1. There were no attempts to get a better concentration ratio but flow rates were monitored twice (Table 11). Four sets of samples were taken: A (1:30 PM) and D (4:30 PM) were complete sets (one from each sampling port, feed and combined concentrate), while B (2:30 PM) and C (3:30 PM) were check samples from port #1 (Toray) and #4 (Filmtec). Tables 12 (A), 13 (B & C) and 14 (D) show the results obtained. At the end of the day the unit was rinsed and cleaned.

On June 28 the unit was moved to another section of the chemical plant to perform a two stage trial on an industrial process waste water stream. It contained, among many chemicals, monoethylene glycol (MEG) and sodium. The unit was first reconfigured with four parallel banks of either 1 or 2 membrane elements (see Figure 1). For the first time the cellulose acetate DSI CA 4021 were used. The purpose of that first configuration was to study the permeates from each one of these membranes.

TABLE 11

RO MEMBRANES FLOW RATES JUNE 27 (Petrochemical Co.)
CHEMICAL LANDFILL LEACHATE

TYPE	FLOW RATES (sec/L)	
	3:00 PM	5:00 PM
2 x Toray permeate port #1	52	55
2 x Toray permeate port #2	51	46
2 x Filmtec permeate port #3	30	31
2 x Filmtec permeate port #4	23	25
Combined permeate	3.1	3.3
Combined concentrate	5.8	5.3

TABLE 12

RO RESULTS FROM THE PETROCHEMICAL CO.
JUNE 27, CHEMICAL LANDFILL LEACHATE

800 PSI 2:1 SET A (1:30 PM)

ANALYSES		RESULTS					
TYPE	UNITS	FEED	MEMBRANES				CONCENTRATE
			TORAY		FILMTEC		
			Port 1	Port 2	Port 3	Port 4	
B	mg/L	1.81	<0.013	<0.013	<0.013	<0.013	2.92
Cu	mg/L	1.71	0.210	<0.03	<0.03	<0.03	3.12
Fe	mg/L	13.23	<0.03	0.043	<0.03	<0.03	21.34
Ni	mg/L	0.44	0.06	<0.05	<0.05	<0.05	0.71
Sr	mg/L	0.35	<0.005	<0.005	<0.005	<0.005	0.45
Mo	mg/L	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Cr	mg/L	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
Al	mg/L	0.75	<0.15	<0.15	<0.15	<0.15	0.87
K	mg/L	<100	<100	<100	<100	<100	<100
Mg	mg/L	5.18	<0.06	<0.06	<0.06	<0.06	8.04
Ca	mg/L	35.7	2.45	1.42	0.82	0.99	56.2
Na	mg/L	8900	289	109	167	166	13900
OH^-	mg/kg	362.1	154.8	54.3	69.3	71.9	561.1
CO_3^{2-}	mg/kg	2043	64	59.6	69.9	92.3	3261
pH	pH units	12.1	11.7	11.3	11.4	11.5	12.2
Conductivity	µS/cm	46000	2400	1000	1000	1400	64000
TOC	mg/L	1800	35.0	25	29	25.8	3000
Cl	mg/L	18000	64	39	79	43	53000
MEG	mg/L	270	57	33	48	35	270
Phenolics	µg/L	270	450	125	250	175	460
TKN	mg/L	67	-	-	-	-	69
Nitrate	mg/L	25	<5	<5	<5	<5	25
Sulphate	mg/L	464	<5	<5	<5	<5	469

TABLE 13

RO RESULTS FROM THE PETROCHEMICAL CO.
JUNE 27, CHEMICAL LANDFILL LEACHATE

800 PSI 2:1 SET B (2:30 PM) AND C (3:30 PM)

ANALYSES		RESULTS				
TYPE	UNITS	FEED	MEMBRANES			
			TORAY (port #1)		FILMTEC (port #4)	
			2:30 PM	3:30 PM	2:30 PM	3:30 PM
B	mg/L	1.81	<0.013	<0.013	<0.013	<0.013
Cu	mg/L	1.71	<0.03	<0.03	<0.03	<0.03
Fe	mg/L	13.23	<0.03	<0.03	<0.03	<0.03
Ni	mg/L	0.44	<0.05	<0.05	<0.05	<0.05
Sr	mg/L	0.35	<0.005	<0.005	<0.005	<0.005
Mo	mg/L	<0.07	<0.07	<0.07	<0.07	<0.07
Cr	mg/L	<0.015	<0.015	<0.015	<0.015	<0.015
Al	mg/L	0.75	<0.15	<0.15	<0.15	<0.15
K	mg/L	<100	<100	<100	<100	<100
Mg	mg/L	5.18	<0.06	<0.06	<0.06	<0.06
Ca	mg/L	35.7	0.92	0.76	0.49	0.52
Na	mg/L	8900	273	309	154	174
OH^-	mg/kg	362.1	161.4	162.3	85.8	91.9
CO_3^{2-}	mg/kg	204.3	58.1	74.1	58.3	52.1
pH	pH Units	12.1	11.7	11.8	11.2	11.5
Conductivity	µS/cm	46000	2200	2100	1000	1200
TOC	mg/L	1800	37	39	31	32
Cl	mg/L	18000	100	82	61	64
MEG	mg/l	270	59	60	38	37
Phenolics	µg/L	270	125	125	100	150
TKN	mg/L	67	-	-	-	-
Nitrate	mg/L	25	<5	<5	<5	<5
Sulphate	mg/L	464	<5	<5	<5	<5

TABLE 14

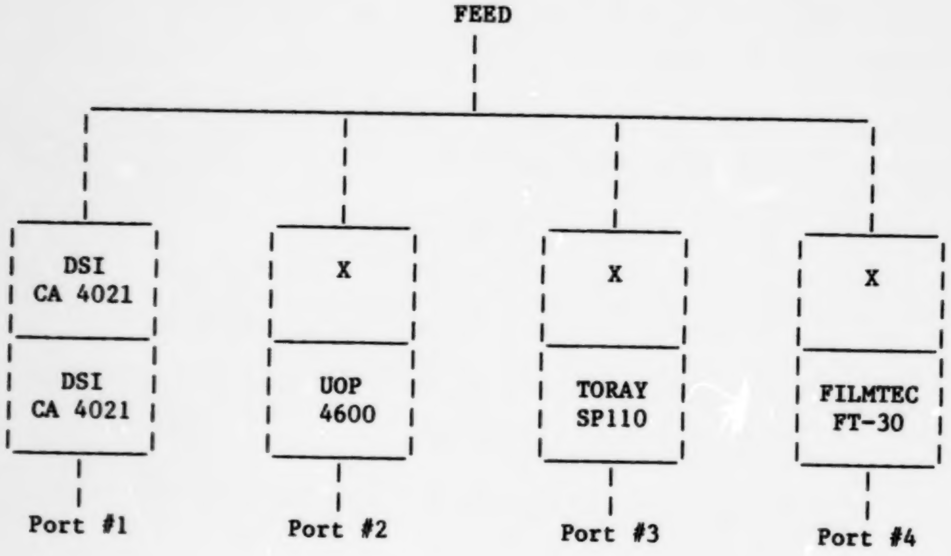
RO RESULTS FROM THE PETROCHEMICAL CO.
JUNE 27, CHEMICAL LANDFILL LEACHATE

800 PSI 2:1 SET D (4:30 PM)

ANALYSES		RESULTS					
TYPE	UNITS	FEED	MEMBRANES				CONCENTRATE
			TORAY		FILMTEC		
			Port #1	Port #2	Port #3	Port #4	
B	mg/L	1.82	<0.013	<0.013	<0.013	<0.013	2.73
Cu	mg/L	1.76	<0.03	<0.03	<0.03	<0.03	2.98
Fe	mg/L	13.31	<0.03	<0.03	<0.03	<0.03	19.49
Ni	mg/L	0.46	<0.05	<0.05	<0.05	<0.05	0.67
Sr	mg/L	0.34	<0.005	<0.005	<0.005	<0.005	0.46
Mo	mg/L	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
Cr	mg/L	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
Al	mg/L	0.55	<0.15	<0.15	<0.15	<0.15	0.56
K	mg/L	<100	<100	<100	<100	<100	<100
Mg	mg/L	5.18	<0.06	<0.06	<0.06	<0.06	<6.12
Ca	mg/L	34.9	0.69	0.89	0.60	0.84	50.2
Na	mg/L	8800	327	139	177	198	13400
OH^-	mg/kg	363.4	175.0	71.0	80.2	94.8	551.4
CO_3^{2-}	mg/kg	1023	60.8	54.4	52.5	66.0	3115
pH	pH Units	12.0	11.8	11.4	11.4	11.5	12.2
Conductivity	μS/cm	44000	2350	1200	1200	1300	63000
TOC	mg/L	1800	39	27	30	33	2800
Cl	mg/L	18000	100	36	68	68	28000
MEG	mg/L	260	63	43	41	42	350
Phenolics	μg/L	310	75	125	200	125	430
TKN	mg/L	66	-	-	-	-	95
Nitrate	mg/L	25	<5	<5	<5	<5	25
Sulphate	mg/L	481	<5	<5	<5	<5	806

FIGURE 1

RO MEMBRANES CONFIGURATION FOR JUNE 28
FIRST PORTION OF THE PROCESS STREAM TRIAL



The permeate of the DSI CA 4021 was to be accumulated in 45 gallon drums and kept for the second portion of that particular trial. By 1:00 PM the unit was ready to go. The membranes were conditioned at 200 PSI for 20 minutes, 400 PSI for 20 minutes and 600 PSI for 20 minutes (600 PSI is the maximum acceptable pressure for the DSI CA 4021). We then started to accumulate the DSI CA permeate. Measures of all the permeate flow rates are shown in Table 15. Three sets of samples were taken from each sampling ports (Table 16). The unit was shut down at 3:30 PM and reconfigured for the second portion (Figure 2).

TABLE 15

RO MEMBRANES PERMEATE FLOW RATES JUNE 28
INDUSTRIAL WASTE STREAM 600 PSI 1:1

PORT #	MEMBRANE TYPE	FLOW RATES (sec/L)
1	2 X DSI CA 4021	3.5
2	1 X UOP 4600	6.9
3	1 X TORAY SP110	26.4
4	1 X FILMTEC FT-30	15

TABLE 16

RO RESULTS FOR THE FIRST PORTION OF THE INDUSTRIAL PROCESS WASTE STREAM JUNE 28/85, 600 PSI 1:1, PETROCHEMICAL CO.

TIME		MEMBRANES (results in ppm)							
		DSI CA 4021		UOP 4600		TORAY SP110		FILMTEC FT-30	
		MEG	SODIUM	MEG	SODIUM	MEG	SODIUM	MEG	SODIUM
2:30 PM	FEED	3490	74	3490	74	3490	74	3490	74
	PERMEATE	3120	4	1970	3	936	3	1450	5
3:00 PM	FEED	3460	74	3460	74	3460	74	3460	74
	PERMEATE	2750	3	1880	2	841	2	1350	5
3:30 PM	FEED	4040	75	4040	75	4040	75	4040	75
	PERMEATE	2485	3	2785	2	727	2	1292	4

On June 29 we did the second portion of the industrial waste water trial which consisted in recirculating the DSI CA 4021 permeate into 4 Filmtec FT-30 membranes at 800 PSI and different concentration ratios. The trial lasted about 1.5 hours. The constant increase of the water temperature prevented us from continuing for a longer period. The results obtained are presented in Table 17. At the end of the day the membranes were rinsed and cleaned and the unit shutdown.

FIGURE 2

RO MEMBRANES CONFIGURATION FOR JUNE 29
SECOND PORTION OF THE INDUSTRIAL PROCESS WASTE WATER

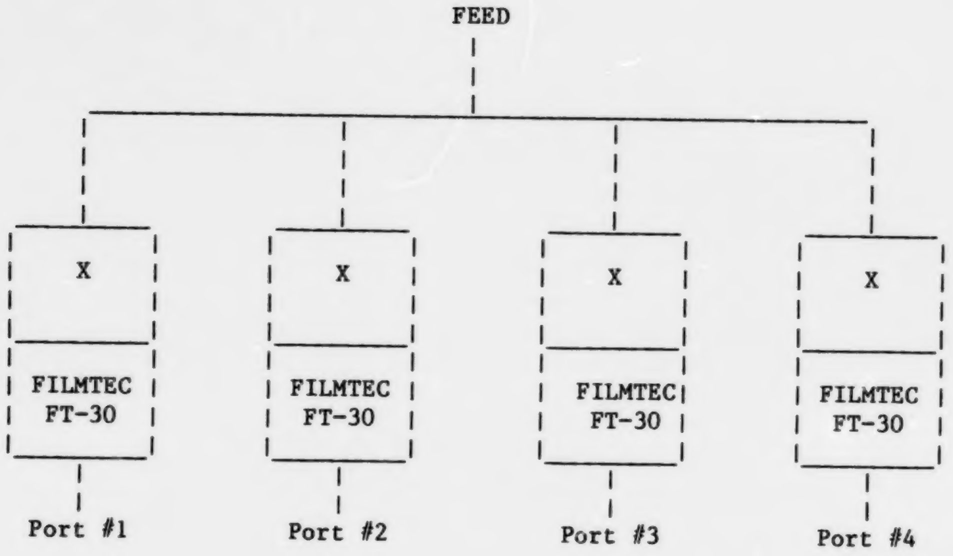


TABLE 17

RO RESULTS FOR THE SECOND PORTION OF THE
INDUSTRIAL PROCESS WASTE STREAM
JUNE 29 800 PSI PETROCHEMICAL CO.

SAMPLE	PERMEATE TO CONCENTRATE RATIO					
	1:1		2:1		6:1	
	MEG	Na	MEG	Na	MEG	Na
Permeate	804	2	580	1	996	1
Concentrate	2507	10	3477	13	3668	14

B. Discussion (Petrochemical Co.)

Landfill Leachate

From past experience (especially Gloucester 1984), we knew that reverse osmosis was capable of handling simultaneously a wide variety of organic and inorganic chemicals. That portion of the trial was then anticipated to be a success. The permeate to concentrate ratio of approximately 2:1 was kept at that level for purely practical reasons. No attempt was made to concentrate the effluent more. The flow rates shown in Table 11 indicates that the flows were very stable throughout the duration of the trial (no plugging). The Filmtec membranes, once again, have proven themselves to be quicker workers than Toray but the results shown in Tables 12, 13 and 14 surprisingly indicates that increases in flow rates do not imply lower rejections.

If we study the results as we go down the Tables we notice the following behaviour: for all the metal ions both with Toray and Filmtec we have a 99.9% removal which means that the membranes were very stable throughout the trial. As far as the sodium is concerned, we obtained only 96% to 98% removal. This is less than what was expected. We attribute the situation to the presence of so many other ions at such concentrations that the membranes were overloaded. Calcium was stable at 98% and so was the carbonate (97%). Hydroxides behaved very strangely with removals of 50% to 80% for Toray and about 75% for Filmtec. Being a small molecule, even if it is hydrated, it was expected that its rejection would be low. The pH was pretty stable at about 11.5 but we noticed that the permeate was less basic than the original solution (probably related to the removals of certain inorganic species). Conductivity was very well handled (96% to 98%) and so was the TOC (98%). Excellent results were obtained for chlorides (99.5%). MEG seemed to be better rejected by Filmtec (86%) than Toray (77%). As far as the phenolics are considered, we obtained surprising results (76%-54%) Toray and (63%-52%) Filmtec. In British Columbia (1984) RO successfully removed chlorophenols up to 2000 ppm, with 99.9% rejections. It was anticipated that similar results would be obtained. It seems that the presence of "Cl" arms on the molecule is determinant. Finally, nitrate, sulphate and TKN presented, as expected, good rejections (up to 99%). The concentrate values match their feed counterparts when the concentration ratio used during the trial is considered.

In conclusion we can say that Filmtec generally speaking presented better flow rates and slightly better rejections than Toray, but both membranes were outstanding.

Industrial Process Waste Stream

That portion of the trial had to be performed in two stages because of the chemicals involved. The waste stream contained monoethylene glycol (MEG) sodium and many other chemicals (organics and inorganics). The problem was to find a way to concentrate that waste stream so that MEG could be disposed of more easily but in absence of sodium.

i) First Stage

Figure 1 describes the configuration used during the first stage of the operation. As we can see two DSI CA 4021 membranes were put in. They were chosen because of their ability to reject sodium but not organic molecules. The permeate obtained from these membranes was accumulated because it contained mostly organic molecules but only traces of inorganics. The UOP 4600 was used as an experiment because it was believed that the membrane could have a behaviour close to the DSI CA 4021. Toray SP110 and Filmtec FT-30 were used to evaluate their rejection capability. The results shown in Table 16 confirmed the expected behaviour of the membranes. In fact, considering that the feed concentration was pretty stable (3500-4000 ppm MEG, 74 ppm Na) we can see that in the case of the DSI CA 4021, between 60% and 90% of the MEG was recovered in the permeate while 96% of the sodium was rejected in the concentrate which means that indeed the cellulose acetate membranes reject the inorganics and let the low molecular weight organics pass. If we plot the concentration of MEG in the permeate against time we see that it decreases steadily. It indicates that probably the membranes were not conditioned long enough. A good extrapolation would probably indicate that between 50% and 70% of the MEG could be recovered with one pass.

The UOP 4600 behaved almost like the cellulose acetate. In fact, the results show a 97% sodium rejection with a 55%-70% recovery of MEG. Here too we notice the instability of the MEG permeate concentration but at this point it indicates that the recovery of this chemical should increase slightly until the membranes are fully conditioned. Also, a quick look at Table 15 indicates that the UOP 4600 flow rate per membrane element is very close to the DSI CA 4021 which reinforces the idea of similar behaviour.

The Toray SP110 shows a salt rejection of 97% and a MEG rejection of 70%-80% which is very good considering the size of MEG (comparable to the landfill results). That high rejection rate is naturally complemented by a low flow rate of 26 sec/L. As for the Filmtec FT-30, it shows a 95% salt rejection and 60-70% MEG rejection which is less than what was expected since we achieved a removal of more than 80% at the landfill site.

As a quick résumé, we can say that all the membranes had a good salt rejection but they all behaved differently with respect to MEG.

ii) Second Stage

Figure 2 describes the unit configuration for the second stage of the operation. We used only Filmtec FT-30. The purpose of that trial was to study how well that membrane could concentrate the MEG from a CA permeate at different concentration ratio (Table 17). It is interpreted from the permeate and concentrate data that the feed concentration for that second stage was lower than what was recorded the day before. (About 1500 ppm instead of 2400 ppm). That situation is probably the result of dilution by residual water present in the equipment. The results show that we concentrated both MEG and sodium. Nevertheless, we were able to get a final solution that contained more than twice the original concentration of MEG but only 13 ppm of sodium. Table 17 also tends to indicate that the effluent quality does change with the concentration ratio. The optimum condition seems to be at 2:1.

CONCLUSIONS

Melville:

- reverse osmosis has proven itself to be a suitable method to treat potash car wash water;
- with percentage of removal of up to 99%, Toray SP110, Filmtec FT-30 and UOP 1001 seem to be excellent membranes to clean up potash water; and
- high temperature (30-37°C) influences the flow rates and permeate quality of most membranes except UOP 1001.

Edmonton:

- reverse osmosis can handle insecticide/herbicide contaminated water with a high level of efficiency; and
- Toray SP110, Filmtec FT-30, UOP 1001 and DSI B441 seems to be very good at cleaning up toxic waste water.

Petrochemical Co.:

- the presence of "Cl" on phenolic compounds appears to be essential to obtain 99% removals;
- reverse osmosis once again demonstrated its applicability to chemical landfill leachate treatment; and
- a two stage reverse osmsosis trial demonstrated that we can separate organic and inorganic contaminants and concentrate them individually.

ACKNOWLEDGEMENTS

We would like to thank Canadian National Railways and the Western and Northern Region of the Environmental Protection Service, as well as the Petrochemical Co. for their financial participation to the project.

We also want to express our gratitude to Clifton Associates and Alberta Environment for the analyses performed on our samples.

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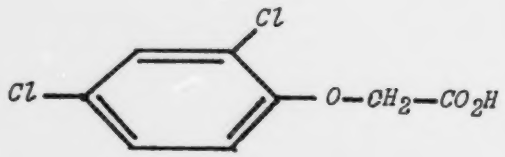
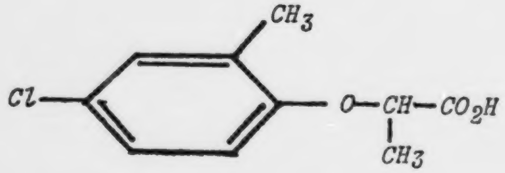
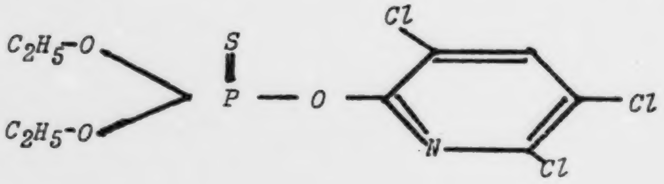
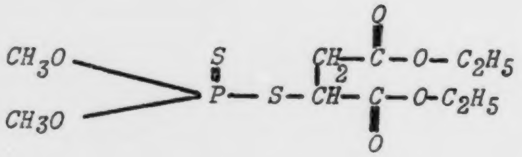
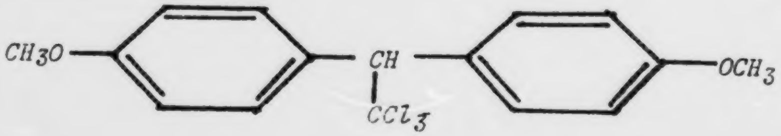
- Reverse Osmosis for Cleanup of Spilled Wood Protection Solution, J.B. Straforelli, H. Whittaker. Environment Canada 1985.
- Concentration of Dilute Chemical Landfill Leachate by Reverse Osmosis, H. Whittaker, Environment Canada, C. Adams, University of Waterloo 1985.

P.S. Cette publication est aussi disponible en Français.

ANNEX A

Name	Chemical Structure
2,4-D	
Mecoprop	
Dursban	
Malathion	
Methoxychlor	

UTILISATION DE L'OSMOSE INVERSE ET DE L'ULTRAFILTRATION AUX MUNICIPALITÉS DE GRANBY ET DE STE-ANNE-DES-PLAINES (QUÉBEC)

Beauregard, B./Tremblay, J.
Ministère de l'Environnement du Québec - Environnement Canada

INTRODUCTION

Les corporations municipales de la ville de Granby et de la paroisse de Ste-Anne-des-Plaines ont indiqué à la Direction régionale de Montréal du ministère de l'Environnement du Québec ainsi qu'au Service de la Protection de l'Environnement d'Environnement Canada, leur désir d'utiliser une unité mobile d'osmose inverse pour fins de démonstrations et/ou d'essais. Les objectifs fixés furent de déterminer et/ou de démontrer l'efficacité avec laquelle l'osmose inverse ou l'ultrafiltration peut traiter les eaux de surface du lac Boivin (Granby) et les eaux souterraines de la région de Ste-Anne-des-Plaines.

Les essais ont eu lieu les 26, 27 et 28 septembre 1984 (Granby) et les 16, 17 et 18 juillet 1985 (Ste-Anne-des-Plaines).

GRANBY

Le ministère de l'Environnement du Québec et Environnement Canada se sont rendus à la station de purification d'eau de Granby en septembre 1984 dans le but de vérifier les résultats des procédés d'ultrafiltration et d'osmose inverse sur le traitement de l'eau brute de la prise d'eau dans le lac Boivin. Le traitement actuel de l'eau brute de surface du lac Boivin, soit une oxydation au bioxyde de chlore, une floculation à l'aide du sulphate d'aluminium et de la silice activée, une désinfection au chlore et un réajustement du pH à l'aide de l'hydroxyde de calcium, s'avère inefficace à produire une eau de qualité acceptable pour la consommation humaine. Nous avons donc évalué les procédés d'ultrafiltration (UF) et d'osmose inverse (OI) comme technologie de rechange.

Pour les procédés d'ultrafiltration et d'osmose inverse, l'eau brute provenait du réservoir de 300 000 000 gallons imp. dans le lac Boivin. Les résultats des analyses physico-chimiques de l'eau brute de cette prise d'eau démontrent que cette eau est ferrugineuse (0.39 mg/L Fe et 0.71 mg/L Mn le 84-09-27 et 0.77 mg/L Fe et 1.03 mg/L Mn le 84-09-28), colorée (18 U.C.V. le 84-09-27 et 66 U.C.V. le 84-09-28) et turbide (100 U.T.N. le 84-09-27 et 30 U.T.N. le 84-09-28), renferme des tannins-lignine (0.4 mg/L), des substances organiques azotées (3.09 mg/L N le 84-09-27 et 1.84 mg/L N le 84-09-28), des substances organiques phosphorées (0.04 mg/L P le 84-09-27), des substances phénoliques (0.003 mg/L le 84-09-27) et des algues (5 400/mL espèces telles que Aphanizomenon le 84-09-27 et 1 270/mL le 84-09-28) et a une demande chimique en oxygène (75 mg/L le 84-09-27 et 65 mg/L le 84-09-28).

L'unité mobile d'Environnement Canada servit au traitement de cette eau brute pour les deux procédés ci-dessus. Différentes membranes furent utilisées, soit des membranes en polysulphone de Desalination Inc. et de FilmTec pour l'ultrafiltration et des membranes en polyamide/polysulphone de FilmTec, en polyéther/amide-polysulphone de UOP, en polyéther-polysulphone de Toray et en polyamide de Desalination Inc. pour l'osmose inverse.

Concernant le premier procédé, la pression a été maintenue à 100 livres/pouce carré aux quatre membranes utilisées. Les résultats des analyses physico-chimiques de l'eau traitée à l'ultrafiltration montrent que les teneurs en fer et en manganèse, les concentrations des substances organiques azotées et phosphorées et les algues ont été complètement éliminées sauf par la membrane de DSI U90 G50 qui a laissé passer plus de la moitié des substances organiques azotées.

La concentration des tannins-lignine a été réduite de 50%, passant de 0.4 mg/L à 0.2 mg/L, et la dureté totale et l'alcalinité totale ont diminué jusqu'à une valeur minimale de 35 mg/L $CaCO_3$ et 28mg/L $CaCO_3$, respectivement. Une alcalinité totale plus petite que 30 mg/L $CaCO_3$ et une dureté totale inférieure à 20 mg/L $CaCO_3$ peuvent créer de multiples problèmes de corrosion au réseau de distribution d'eau lorsque le pH de l'eau se situe plus bas que 6.5.

L'eau traitée à l'ultrafiltration renferme une certaine teneur en tannins-lignine et ce fait occasionne une demande du carbone organique total, soit une valeur de 1.5 à 2 mg/L. Finalement, cette eau brute colorée et turbide est devenue incolore et limpide et renfermait toutefois une odeur, probablement attribuable à la présence des tannins-lignine dans l'eau traitée.

Par le procédé d'osmose inverse à une pression aux quatre membranes utilisées de 810 livres/pouce carré, la plupart des éléments minéraux, des substances organiques et des anions inorganiques a été enlevée ou réduite à l'état de trace. Seuls les tannins-lignine n'ont pu être complètement éliminés, passant d'une concentration de 0.4 mg/L à 0.1 mg/L dans l'eau traitée.

Conclusion (Granby)

1- L'eau brute du réservoir de 300 000 000 gal. imp. dans le lac Boivin contient du fer et du manganèse. Cette réserve d'eau de surface renferme des matières organiques reliées aux tannins-lignine et à des substances organiques azotées et phosphorées. De plus, une grande quantité d'algues est dénombrée dans cette eau, soit une algue bleue de l'espèce Aphanizomenon et quelques diatomées dont l'espèce Navicula.

2- L'ultrafiltration, procédé de séparation par membranes semi-perméables sous l'effet d'une pression, retient les particules insolubles (les algues et les substances causant la turbidité), des ions dissous (le fer et le manganèse en particulier) et également des molécules dissoutes (substances organiques azotées et phosphorées et une partie des tannins-lignine).

3- L'ultrafiltration, qui utilise la propriété des membranes en polysulphone (perméables à l'eau et aux ions de la dureté mais imperméables aux particules et à certains solutés), constitue un procédé valable pour éliminer des matières dissoutes dans l'eau brute des prises d'eau de la station de purification de Granby pour la rendre potable.

4- Une pression de l'ordre de 100 livres/pouce carré est suffisante pour retenir la plupart des matières dissoutes indésirables dans l'eau brute.

5- L'osmose inverse, procédé qui force l'eau à passer à travers une membrane sélective semi-perméable, permet la rétention des ions inorganiques et des matières organiques dissoutes et en suspension dans l'eau brute du réservoir dans le lac Boivin.

6- Le traitement actuel à la station de purification d'eau par les procédés d'oxydation au bioxyde de chlore, de précipitation au sulfate d'aluminium, de sédimentation et de filtration ne permet pas d'éliminer complètement les substances organiques phosphorées et les tannins-lignine.

7- Le traitement chimique de l'eau brute du réservoir dans le lac Boivin ne permet pas de rencontrer toutes les normes chimiques et les limites des autres paramètres recommandés pour l'eau potable.

8- Le traitement physique proposé comprend le procédé d'ultrafiltation de l'eau brute, la filtration de l'eau claire sur du charbon actif, la désinfection de l'eau filtré au chlore et le réajustement du pH de l'eau traitée à l'aide de l'hydroxyde de calcium si nécessaire avant sa distribution dans le réseau d'aqueduc municipal. Pour les unités d'ultrafiltration, les membranes en polysulphone DSI U90 G20 sont recommandées pour le traitement de cette eau brute.

TABLEAU 1
ANALYSES MICROBIOLOGIQUES DES ÉCHANTILLONS PRÉLEVÉS À GRANBY

Date	Lieu du prélèvement	Algues	Concentration
84-09-27	Eau brute - réservoir 300 000 000 gal. imp.	Aphanizomenon	5 400/mL
84-09-27	Eau traitée (ultrafiltration)		
	DSI U90 G 10		-*
	DSI U90 G 20		-
	DSI U90 G 50		-
	Filmtec UFP		-
84-09-27	Rejet	Navicula, Aphanizomenon	3 300/mL
84-09-28	Eau brute - réservoir 300 000 000 gal. imp.		1 270/mL
84-09-28	Eau traitée (osmose inverse)		
	Filmtec FT 30		-
	UOP 1001		-
	Toray SP 110		-
	DSI B 441		-

* -: négatif

TABLEAU 2
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À GRANBY (UF)

		mg/L						mg/L $CaCO_3$		mg/L N		mg/L P	
Date	Lieu du prélèvement	Ca	Fe	K	Mg	Mn	Na	Dureté Totale	Alc. Totale	Azote total	Azote Ammo.	Phosph. total	Phos. total inorg.
84-09-27	Eau brute - Réservoir prise d'eau Lac Boivin	16.2	0.39	2.4	3.5	0.71	9.3	55	40	3.1	0.01	0.2	0.16
84-09-27	Eau traitée par ultrafiltration DSI U90 G10	11.2	<0.05	1.8	2.5	0.01	8.0	38	32	<0.1	0.02	<0.1	<0.02
84-09-27	DSI U90 G20	10.1	<0.05	1.6	2.4	<0.01	7.7	35	28	<0.1	0.02	<0.1	<0.02
84-09-27	DSI U90 G50	12.5	<0.05	1.9	2.8	<0.01	8.9	42	34	1.6	0.02	<0.1	<0.02
84-09-27	Filmtec UFP	14.8	<0.05	2.1	3.2	0.01	9.3	50	35	<0.1	0.02	<0.1	<0.02

TABLEAU 2 (suite)
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À GRANBY (UF)

		mg/L				µ mhos	U.C.V.		U.T.N.	mg/L	mg/L	mg/L
Date	Lieu du prélèvement	SO_4	Cl	COT	DCO	Conductivité	Couleur	pH	Turbidité	Solides dissous	Phénols	Tannins-lignine
84-09-27	Eau brute - Réservoir prise d'eau - Lac Boivin	17	14		75	170	18	7.3	100	115	0.003	0.4
84-09-27	Eau traitée par ultrafiltration DIS U90 G10	4	12	1.5	<10	120	5	7.6	0.1	65	0.002	0.2
84-09-27	DSI U90 G20	6	10	1.5	<10	110	2	7.7	0.1	61	<0.002	0.2
84-09-27	DSI U90 G50	8	12	2	<10	130	2	7.5	0.1	77	<0.002	0.2
84-09-27	Filmtec UFP	11	14	*ND	<10	140	5	7.9	0.1	77	<0.002	0.3

* ND: non disponible

TABLEAU 3
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À GRANBY (OI)

		mg/L						mg/L $CaCO_3$		mg/L N		mg/L P	
Date	Lieu du prélèvement	Ca	Fe	K	Mg	Mn	Na	Dureté Totale	Alc. Totale	Azote total	Azote Ammo.	Phosph. total	Phos. total inorg.
84-09-28	Eau brute - réservoir 300 000 000 gallons - Lac Boivin	20.2	0.77	2.9	5.4	1.03	14.1	72	65	2	0.16	0.1	0.1
84-09-28	Eau traitée par osmose inverse Filmtec FT 30	0.4	<0.05	0.2	0.1	<0.01	1.1	<1	3	<0.1	0.02	<0.1	<0.02
84-09-28	UOP 1001	0.7	<0.05	0.6	0.2	<0.01	2.9	<1	4	<0.1	0.02	<0.1	<0.02
84-09-28	Toray SP 110	0.1	<0.05	0.2	<0.1	<0.01	1.8	<1	3	<0.1	0.02	<0.1	<0.02
84-09-28	DSI B441	0.2	<0.05	0.4	0.1	<0.01	3.5	<1	6	<0.1	0.02	<0.1	<0.02

TABLEAU 3 (suite)
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À GRANBY (OI)

		mg/L				µ mhos	U.C.V.		U.T.N.	mg/L	mg/L	mg/L
Date	Lieu du prélèvement	SO_4	Cl	COT	DCO	Conductivité	Couleur	pH	Turbidité	Solides dissous	Phénols	Tannins-lignine
84-09-28	Eau brute - réservoir 300 000 000 gallons - Lac Boivin	11	22		65	240	66	6.9	30	129	<0.002	0.4
84-09-28	Eau traitée par osmose inverse Filmtec FT 30	<1	<2	<0.5	<10	10	<2	6.3	<0.1		<0.002	<0.1
84-09-28	UOP 1001	<1	8	<0.5	<10	18	<2	6.3	<0.1		<0.002	0.1
84-09-28	Toray SP 110	<1	<2	1	<10	10	<2	6.3	<0.1		0.002	0.1
84-09-28	DSI B441	<1	<2	<0.5	<10	15	<2	6.7	<0.1		<0.002	0.1

STE-ANNE-DES-PLAINES

Le ministère de l'Environnement du Québec et Environnement Canada se sont rendus à la station de chloration de Ste-Anne-des-Plaines en juillet 1985 dans le but de vérifier les résultats du procédé d'osmose inverse sur le traitement des puits tubulaires municipaux. L'unité mobile d'Environnement Canada servit au traitement de ces eaux brutes.

Différentes membranes furent utilisées, soit des membranes en acétate de cellulose et en polyamide de Desalination Inc., des membranes en polyéther/amide-polysulphone de UOP, des membranes en polyéther-polysulphone de Toray et des membranes en polyamide - polysulphone de FilmTec.

Les premiers essais furent effectués sur l'eau brute des puits tubulaires no. 1, 2 et 5. La pression a été maintenue à 250 livres/pouce carré aux quatre membranes utilisées et 50% du débit était rejeté. La membrane en acétate de cellulose 4021 de DSI a donné de très bons résultats en éliminant complètement les teneurs en fer et en manganèse, les concentrations des substances organiques azotées et phosphorées et la couleur. Le seul inconvénient est l'élimination de la dureté et de l'alcalinité du mélange de l'eau souterraine des trois puits, qui est compensée par une réduction importante de la teneur en sodium, de la conductivité et des solides dissous. Finalement, le débit à travers les deux membranes de 4 pouces de diamètre installées en série est excellent, soit de l'ordre de 3 L/min.

La même expérience a été reprise en augmentant la pression à 280 livres par pouce carré et en réduisant le rejet à 11%. Les mêmes résultats ont été obtenus que précédemment.

Pour le puits no. 8, la pression a été maintenue à 340 livres/pouce carré aux quatre membranes utilisées et le rejet a été fixé à 9%. Les résultats des analyses physico-chimiques de l'eau traitée à l'osmose inverse montrent que les teneurs en sodium, les concentrations des substances organiques phosphorées, les tannins-lignine et la couleur ont été complètement éliminées. La membrane en polyéther/amide-polysulpone 4600 de UOP a donné le meilleur rendement quant au débit à travers les deux membranes mais a laissé passer complètement l'azote ammoniacal et 25% du sodium.

Concernant le puits d'essai (no. 9), un procédé à deux étapes a été essayé, soit en faisant passer l'eau souterraine à travers deux membranes en acétate de cellulose dans la première étape et l'eau traitée à travers d'autres membranes d'un autre type dans la seconde étape. Cette façon de procéder n'a pas augmenté la qualité de l'eau traitée, car après la première étape, un très bon rendement est atteint, soit une réduction importante du sodium, de la conductivité et des solides dissous et une élimination des substances organiques phosphorées, des tannins-lignine et de la couleur. La membrane en acétate de cellulose 4021 de DSI est recommandée du point de vue débit (3 L/min) et du point de vue rendement du traitement.

Conclusion

1- L'eau brute des puits no. 1 et 2 renferme une teneur en fer et en manganèse supérieure à la norme de qualité de l'eau potable, soit 0.3 mg/L Fe et 0.05 mg/L Mn, respectivement.

2- L'eau brute des quatre puits tubulaires et d'essai renferme une teneur en sodium supérieure à 115 mg/L Na. Dans les puits no. 8 et d'essai, l'eau souterraine est considérée salée.

3- L'eau brute des puits no. 2 et 5 est considérée dure puisque la dureté totale est supérieure à 200 mg/L $CaCO_3$.

4- L'eau brute des quatre puits tubulaires et d'essai renferme des matières organiques reliées aux tannins-lignine, soit de l'ordre de 0.9 à 1.9 mg/L.

5- L'eau brute des puits d'essai no. 9 et 8 contient aussi des substances organiques azotées et phosphorées.

6- L'osmose inverse, procédé de séparation par membranes semi-perméables sous l'effet d'une pression, retient les particules insolubles (les substances causant la turbidité), des ions dissous (sodium) et également des molécules dissoutes (substances organiques azotées et phosphorées et tannins-lignine).

7- L'osmose inverse, qui utilise la propriété des membranes en acétate de cellulose (perméables à l'eau mais imperméables aux particules et à certains solutés), constitue un procédé valable pour éliminer des matières dissoutes dans l'eau souterraine des puits tubulaires de la paroisse de Ste-Anne-des-Plaines pour la rendre potable.

8- Un traitement physique comprenant une tour d'aération pour le dégagement de l'hydrogène sulfuré et le procédé d'osmose inverse pour un enlèvement complet des substances organiques azotées et phosphorées et une réduction importante de la teneur en sodium s'avère un mode de traitement valable pour l'eau souterraine des puits tubulaires municipaux. Pour les unités d'osmose inverse, les membranes en acétate de cellulose DSI CA 4021 sont recommandées.

TABLEAU 4
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À STE-ANNE-DES-PLAINES
(Puits No. 1, 2 et 5, 250 lb/po^2)

		mg/L						mg/L $CaCO_3$		mg/L N		mg/L P	
Date	Lieu du prélèvement	Ca	Fe	K	Mg	Mn	Na	Dureté Totale	Alc. Totale	Azote total	Azote Ammo.	Phosph. total	Phos. total inorg.
85-07-16	Puits tubulaire no. 1	36.4	0.32	12.9	21.1	0.05	135	178	350	0.9	0.9	0.8	0.8
85-07-16	Puits tubulaire no. 2	50.6	0.37	13.3	24.4	0.08	147	227	360	0.9	0.96	0.8	0.8
85-07-16	Puits tubulaire no. 5	43.	0.21	12.6	24.6	0.05	115	209	360	1.1	1.	0.8	0.8
85-07-16	Mélange des trois puits tubulaires	43.	0.31	11.7	22.5	0.06	127	200	360	1.5	0.8	2.3	0.8
85-07-16	Membrane Acétate de cellulose DSI CA 4021	0.6	<.05	0.8	0.3	<.01	10.5	3	10	<.1	0.1	<.1	<.02
85-07-16	Membrane polyamide DSI TFC B441	0.2	<.05	0.4	0.1	<.01	5.2	1	5	0.1	0.12	<.1	<.02
85-07-16	Membrane polyéther/ amide-polysulphone UOP TFC 4600	0.7	<.05	0.6	0.4	<.01	6.2	3	10	0.5	0.48	<.1	0.02
85-07-16	Membrane polyamide - polysulphone FILMTEC FT-30	4.7	<.05	1.3	2.4	<.01	16.5	22	36	<.1	0.08	<.1	0.08

TABLEAU 4 (suite)
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À STE-ANNE-DES-PLAINES
(Puits No. 1, 2 et 5, 250 lb/po^2)

		mg/L					µ mhos	U.C.V.		U.T.N.	mg/L	mg/L	mg/L
Date	Lieu du prélèvement	SO_4	Cl	F	S	DCO	Conductivité	Couleur	pH	Turbidité	Solides dissous	Phénols	Tannin lignine
85-07-16	Puits tubulaire no. 1	39	56	0.8	0.24	<20	790	30	7.7	0.3	475	<0.003	0.9
85-07-16	Puits tubulaire no. 2	70	68	0.7	0.06	<20	900	30	7.8	0.6	540	<0.003	1.7
85-07-16	Puits tubulaire no. 5	45	54	0.8	0.08	<20	810	26	7.9	0.4	470	<0.003	1.
85-07-16	Mélange des trois puits tubulaires	53	62	0.8		20	850	30	8.	0.9	505		1.
85-07-16	Membrane Acétate de cellulose DSI CA 4021	<1	10	<.1		<20	30	<2	7.1	0.2	45		<.1
85-07-16	Membrane polyamide DSI TFC B441	<1	<2	<.1		<20	<10	<2	6.5	0.2	22		<.1
85-07-16	Membrane polyéther/amide-polysulphone UOP TFC 4600	<1	<2	<.1		<20	35	<2	6.5	0.1	22		<.1
85-07-16	Membrane polyamide-polysulphone FILMTEC FT-30	5	6	0.1		40	110	4	7.1	0.2	67		<.1

TABLEAU 5
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À STE-ANNE-DES-PLAINES
(Puits No. 1, 2 et 5, 280 lb/po^2 et puits No. 8, 340 lb/po^2)

		mg/L						mg/L $CaCO_3$		mg/L N		mg/L P	
Date	Lieu du prélèvement	Ca	Fe	K	Mg	Mn	Na	Dureté Totale	Alc. Totale	Azote total	Azote Ammo.	Phosph. total	Phos. total inorg.
85-07-16	Membrane DSI CA 4021	1.	<.05	2.1	0.6	<.01	22.3	5	20	0.3	0.29	<.1	<.02
85-07-16	Membrane DSI TFC B 441	0.6	<.05	0.7	0.4	<.01	8.9	3	15	<.1	<.07	<.1	0.02
85-07-16	Membrane UOP TFC 4600	0.7	<.05	1.9	0.4	<.01	16.5	3	25	0.2	0.12	<.1	0.02
85-07-16	Membrane FILMTEC TFC FT-30	16.7	<.05	4.7	9.	0.02	51.1	79	115	<.1	0.07	0.5	0.1
85-07-17	Puits tubulaire no. 8	7.5	<.05	16.2	13.7	<.01	243	75	433	1.	0.9	2.6	2.1
85-07-17	Membrane polyéther/ amide - polysulphone UPO TFC HF-1001	0.2	<.05	1.6	0.3	<.01	17.1	2	18	0.9	0.89	<.1	<.02
85-07-17	Membrane DSI TFC B441	0.2	<.05	1.4	0.3	<.01	22.6	2	38	<.1	0.05	<.1	0.02
85-07-17	Membrane UOP TFC 4600	0.2	<.05	5.7	0.3	<.01	54.1	2	63	1.1	1.1	<.1	<.02
85-07-17	Membrane polyéther - polysulphone TORAY SP110	<.1	<.05	0.7	<.1	<.01	9.5	<1	18	<.1	0.02	0.1	0.1

TABLEAU 5 (suite)
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À STE-ANNE-DES-PLAINES
(Puits No. 1, 2 et 5, 280 lb/po^2 et puits No. 8, 340 lb/po^2)

		mg/L					µ mhos	U.C.V.		U.T.N.	mg/L	mg/L	mg/L
Date	Lieu du prélèvement	SO_4	Cl	F	S	DCO	Conductivité	Couleur	pH	Turbidité	Solides dissous	Phénols	Tann lignir
85-07-16	Membrane DSI CA 4021	<1	18	<.1		<10	105	<2	6.7	0.2	60		<.1
85-07-16	Membrane DSI TFC B 441	1	< 2	<.1		<20	45	<2	6.6	0.2	28		<.1
85-07-16	Membrane UOP TFC 4600	<1	6	<.1		<20	25	<2	6.7	0.1	50		<.1
85-07016	Membrane FILMTEC TFC FT-30	21	22	0.3		<10	350	8	7.7	1.5	191		0.2
85-07-17	Puits tubulaire no. 8	4	122	1.5	0.64	14	1130	48	8.2	0.2	655	0.004	1.9
85-07-17	Membrane polyéther/ amide - polysulphone UPO TFC HF-1001	<1	18	<.1		<20	130	<5	6.8	0.1	90		<.1
85-07-17	Membrane DSI TFC B441	<1	10	0.1		<20	118	<5	7.2	0.1	91		<.1
85-07-17	Membrane UOP TFC 4600	<1	56	0.2		<10	309	<2	7.3	0.1	180		<.1
85-07-17	Membrane TORAY SP110 polyéther - polysulphone	<1	< 2	<.1		<20	54	<5	6.6	0.2	44		<.1

TABLEAU 6
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À STE-ANNE-DES-PLAINES
(Puits No. 9, 250 lb/po^2 (17/07) et 270 lb/po^2 (18/07))

Date	Lieu du prélèvement	mg/L						mg/L $CaCO_3$		mg/L N	
		Ca	Fe	K	Mg	Mn	Na	Dureté Totale	Alc. Totale	Azote total	Azote Ammo.
85-07-17	Puits tubulaire no. 9	22.6	0.06	19.2	20.6	<.01	423	141	380	0.5	0.24
85-07-17	Membrane UOP TFC HF-1001	0.3	<.05	1.	0.2	<.01	14.6	1	<5	0.4	0.33
85-07-17	Membrane DSI TFC B-441	0.5	<.05	1.	0.4	<.01	21.7	3	12	<.1	0.06
85-07-17	Membrane UOP TFC 4600	0.4	<.05	2.6	0.4	<.01	36.5	3	15	0.9	0.72
85-07-17	Membrane DSI CA 4021	0.6	<.05	3.7	0.5	<.01	61.5	4	12	0.5	0.46
85-07-18	Membrane UOP TFC HF-1001	0.2	<.05		<.1	<.01	5.6	<1	<5	0.5	0.36
85-07-18	Membrane DSI TFC B-441	0.1	<.05		<.1	<.01	7.2	<1	<5	<.1	<.02
85-07-18	Membrane UOP TFC 4600	0.3	<.05		<.1	<.01	17.1	1	<5		0.58
85-07-18	Membrane FILMTEC FT-30	0.1	<.05		<.1	<.01	2.5	<1	<5		<.02

TABLEAU 6 (suite)
ANALYSES PHYSICO-CHIMIQUES DES ÉCHANTILLONS PRÉLEVÉS À STE-ANNE-DES-PLAINES
(Puits No. 9, 250 lb/po^2 (17/07) et 270 lb/po^2 (18/07))

		mg/L P		mg/L					µ mhos	U.C.V.		U.T.N.	mg/L	mg/L	mg/L
Date	Lieu du prélèvement	Phosph. total	Phos. total inorg.	SO_4	Cl	F	S	DCO	Conductivité	Couleur	pH	Turbidité	Solides dissous	Phénols	Tannins lignine
85-07-17	Puits tubulaire no. 9	2.	1.9	17	540	4.2	4.8	20	2300	45	8.1	1.4	1300	<0.003	1.5
85-07-17	Membrane UOP TFC HF-1001	<.1	<.2	<1	24	0.1		<20	162	<5	6.8	1.2	57		<.1
85-07-17	Membrane DSI TFC B441	<.1	0.06	6	26	0.2		<20	132	<5	6.8	0.2	77		0.2
85-07-17	Membrane UOP TFC 4600	<.1	<.02	<1	58	0.1		<10	229	30	7.	0.3	127		<.1
85-07-17	Membrane DSI CA 4021	<.1	<.02	4	96	0.1		<20	368	<5	6.8	0.1	191		<.1
85-07-17	Membrane UOP TFC HF-1001	<.1	<.02	<1	8	<.1		<20	37	<5	6.1	0.1	28		<.1
85-07-17	Membrane DSI TFC B441	0.3	<.02	1	6	<.1		<20	38	<5	6.5	0.3	32		<.1
85-07-18	Membrane UOP TFC 4600			<1	26	<.1		<20	95	<5	6.5	0.2	53		0.1
85-07-18	Membrane FILMTEC FT-30			1	<2	<.1		<20	15	<5	6.3	0.2	15		0.2

IN-SITU TREATING AGENTS FOR CHEMICAL SPILLS

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Background

Treating agents have been widely proposed in the literature for the in-situ control of spills of hazardous materials. While several reagents have undergone limited laboratory testing specific for toxicity or chemical reactivity, it is apparent that a comprehensive assessment has not been undertaken for many candidate agents which considers a range of practical response concerns. The purpose of this study was to evaluate, on a preliminary basis, treatment techniques commonly referred to in handbooks and other reference documents and potentially applicable to priority substances specified by the Environmental Protection Service (EPS).

Approach

Four tasks were planned in order to achieve the objectives of this project:

Task 1	Identification of Candidate Treating Agents
Task 2	Preliminary Assessment of Treating Agents
Task 3	Laboratory Evaluations
Task 4	Analysis of Data, Reporting

Task 1 Identification of Candidate Agents

An initial review was conducted of the literature to determine standard classifications of treatment methods, possible criteria for either rejecting or selecting chemicals for in-situ use, and the specific chemicals which should be examined as initial candidate agents. As outlined in the terms of reference for this work, the following approaches were to be excluded from consideration:

- acid/base neutralizing agents;
- physical agents such as sorbents;

- activated carbon and charcoal;
- biological agents;
- agents which simply alter the location or state such as simple gelling agents or herders;
- solvents or diluters;
- burning agents; and
- commonly used industrial methods or processes, where the in-situ application would not be new.

This phase of the study involved an examination of manuals, handbooks, technical papers, reports and conference proceedings containing information on chemical spill response and treatment methods. The excellent reference section of the Environmental Emergencies Technology Division (EETD) in Ottawa was directly consulted. It was determined from this literature search that only a limited number of chemical agents are commonly noted that are outside of the list of exclusions specified in the terms of reference for this study. Most of these are discussed in the Noyes Data Corp. spill cleanup text (Robinson 1979). Furthermore, spill response manuals and handbooks usually advocate the flushing, diking, sorption and/or ultimate physical removal of the spilled material and not so much its in-situ treatment. The exception are those spill incidents where neutralization of an acid or base can be readily effected. Nonetheless, the following groups of candidate agents were identified to warrant further investigation:

Precipitation

(1) Clarifying Agents
  - oxalates
  - treated bentonite (clay)

(2) Chelating Agents
  Sequestrants
    - EDTA (alternatives NTA, HEDTA, DPTA, CDTA, etc.)
  Precipitants
    - oxine

Oxidation/Reduction

(1) Oxidants
  - ozone
  - peroxides (hydrogen, calcium, sodium)

(2) Reductants
  - calcium sulfite

Others

(1) Ion Exchange Resins
(2) Organic Polyelectrolytes (alginic acid)

Categorizing agents was found to be an arbitrary process which differs amongst various references and does not usually exclude some overlap of groupings. In addition to the problem of sorting out and conveniently assigning promising agents according to specific physical and chemical processes, it was also somewhat difficult to ignore the expansive knowledge base recently developed for chemical neutralization methods as well as the application of standard wastewater treatment techniques to spills. Both of these latter approaches, however, were exluded from this study as per the directives provided by EETD.

One aspect to which some attention was devoted during the selection process was the applicability of candidate agents to specific priority hazardous substances. Even within the EPS priority lists, toxins were more closely considered in this regard such as cyanides, phenols, aldehydes, metals, etc. rather than the relatively more innocuous materials listed such as sodium chloride and carbon dioxide.

Another component of the selection process was the discussion of candidate agents from different perspectives of individual study team members. In several brainstorming sessions, each person drew upon his or her experience in identifying agents that were (a) amenable to laboratory experimentation, (b) applicable to substances known to pose a significant hazard when spilled, or (c) that would not obviously introduce complications if used at an accident site.

It was at once recognized that while some candidate agents might prove to present difficulties of utilization of one sort or another, several such reagents would be initially included to result in a more comprehensive and encompassing study. Moreover, the subsequent screening process of the next task would eliminate chemical agents that should not be laboratory tested.

Task 2 Preliminary Assessment of Agents

An assessment of the candidate treating agents was then undertaken according to three aspects of their use, namely, chemical reactivity, toxicity, and field practicability.

Chemical Reactivity

The interaction between the candidate treating agents and selected priority substances was hypothesized for reactions that go to completion, simultaneous side reactions, and competing and/or reverse reactions. By examining the literature during this phase of the study, major complicating factors became apparent for some reagents. These factors included the formation of unstable compounds, the possibility of violent or excessive reactions, pH adjustments to allow the desirable reaction to proceed, and the effect of other parameters such as temperature, alkalinity, the presence of organics, etc. Several of the agents studied are briefly discussed.

EDTA

EDTA (or ethylenediamine - tetraacetic acid) is an example of a synthetic aminocarboxylic acid. It is usually sold as disodium salt, but can also be obtained as a free acid, tri- or tetrasodium salt, or as a calcium salt.

Reactions with metals are relatively straightforward and the complexes are very stable. The EDTA anion (Y^{4-}) is a hexadentate complexing agent that complexes a metal ion by "surrounding" it with its two N atoms and its four oxygen atoms. One EDTA molecule binds with one metal ion. The resulting complex is soluble.

i.e. for copper

$$\underset{\text{(disodium EDTA)}}{Cu^{++} + Na_2H_2Y} \longrightarrow CuY^{=} + 2Na + 2H^{+}$$

There are no known "side" reactions. EDTA will bind with other metals present in an aquatic environment and the efficiency of chelation increases as follows:

$$\underset{\text{(least efficient)}}{Mg} < Ca < Fe < Cd < Zn < Ni < \underset{\text{(most efficient)}}{Cu}$$

The chelation of magnesium, calcium and iron (the most predominant metals in the aquatic environment) requires a pH of 10 or more. Therefore, the use of EDTA to complex an element such as copper will not be hampered by the presence of calcium and magnesium.

Ozone

Ozone (O_3) is a colourless gas that is normally formed from oxygen (or air) by electric discharge, U.V. irradiation, or chemical reaction. It is an exceptionally powerful oxidizing agent with a redox potential exceeded only by fluorine.

With inorganic substances, it is not difficult to predict the ultimate end-products of oxidation by ozone. The reactions for ozonation of cyanide are shown below:

$$CN^- + O_3 \longrightarrow \underset{\text{(cyanate)}}{OCN^-} + O_2$$

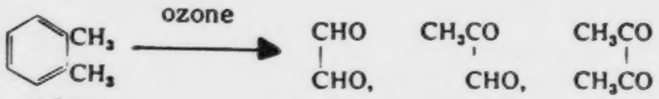
$$OCN^- + 2H^+ + H_2O \longrightarrow CO_2 + \underset{\text{(ammonium ion)}}{NH_4{}^+}$$

$$NH_4{}^+ + OCN^- \longrightarrow NH_4CONH_2$$

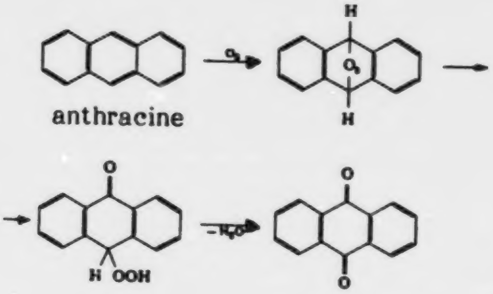
$$NH_2CONH_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

$$NH_2CONH_2 + O_3 \longrightarrow N_2 + CO_2 + 2H_2O$$

With organic compounds, oxidation with ozone can yield a multitude of end-products, some of which are difficult to predict. It is important to apply the ozone in excess. A few examples are noted below:



xylene glyoxyl pyruvaldehyde biacetyl



anthracine

anthraquinone

Sulfite

One of the more promising reducing agents appears to be sulfite ($SO_3^{=}$) which can be obtained in numerous salt forms:

calcium or sodium sulfite
calcium or sodium bisulfite
sodium metabisulfite
etc.

The reaction with sulfite is relatively straightforward,

i.e. to reduce chlorine:

$$SO_3^{=} + Cl_2 \longrightarrow 2Cl + SO_4^{=}$$

Deleterious side reactions are not considered to be a problem. Other candidate treating agents were evaluated in a similar manner as those noted above.

Toxicity

Two separate components of toxicity were originally foreseen as requiring examination. These were mammalian and aquatic toxicological assessments. However, it became apparent during the course of the work that water-based spills, and therefore aquatic-related impacts, were the main area of focus so that terrestrial/mammalian responses to the addition of reagents became less of a concern.

Unreacted reagent, predicted end-products and possible by-products were all examined for their potential toxicity. Two sources which provided much useful information were the water quality criteria compiled for the California State Water Resources Control Board (McKee and Wolf 1976) and the Journal of Environmental Science and Health. Other provincial water quality criteria (Clark 1980) and technical journals were also consulted, as is subsequently noted. Complexans and ozone are now very briefly discussed in terms of the toxicity aspects examined to illustrate the approach taken:

> The literature contains an abundance of experimental work on the use of chelating agents including EDTA, NTA and DTPA (Muramoto 1981, 1982 and 1983). Complexans have been clearly shown to decrease the mortality rate of carp exposed for 100-day test periods to copper, nickel chloride, nickel sulfate, chromium chloride and chromium sulfate. Certainly there are also toxicities associated with the chelating agents themselves (as well as the resultant metal complexes) and the literature reports these usually in conjunction with water quality criteria. For example, fingerling channel catfish succumbed to EDTA at 316 mg/L (McKee and Wolf 1976).
>
> Ozone is not exempt from such examination, and studies show the comparitive toxic effects of ozone on larvae and on eggs as well as on fully developed salmonids (Asbury and Coler 1980; Wedemeyer, Nelson and Yasutaka 1979). Fish larvae can be killed by virtually any measurable residual ozone, whereas eggs remain protected for short exposures, and fully developed rainbow trout tested at lethal threshhold levels of 8 ug/L.

A choice will, no doubt, have to be made on a case-by-case basis as to the advisability of possibly reducing the potential impact of a chemical spill by introducing a reagent that is itself somewhat toxic, albeit considerably less than the substance to which it would be applied. The final report describing this study will summarize the toxicity data which were compiled and reviewed during the course of this work.

Field Practicability

One important aspect of utilizing chemical reagents is the feasibility of transporting and applying them at the spill site. In this regard, the following aspects were examined:

- availability, including grade/purity
- format (gas, liquid, solid, etc.)
- required dosage (or volume)
- physical/chemical properties (solubility, reactivity, corrosivity, affinity for moisture, etc.)
- shelf life, other storage requirements
- safety aspects
- response/reaction time
- application hardware and materials
- cost.

It has been assumed, then, that opportunities might arise to consider the application of reagents, much as neutralization operations have been implemented to control releases of acids and bases. It must, however, be noted that complicating circumstances will occur in spite of this pre-spill investigation of practical aspects. Treatment might not be possible, for example, in the event of a very soluble substance being released into a watercourse; in the case where a high stream velocity transports the material downstream; in the event that it sinks; or where limited access exists. The basic cleanup phases of containment, removal, transfer, storage and/or disposal will still have to be considered in many cases. The presence of organics, suspended sediments and other factors add further complexities to responding to chemical spills with reagents.

Generally, it was found that reagents such as chelating agents, bentonite and sulfites could be readily obtained and broadcast on spills, whereas more exotic treatment systems such as ozone generators would be much more expensive to use and more limited in scope.

Task 3 Laboratory Evaluations

Once candidate agents had been assigned an overall rating, the design of laboratory experiments was initiated. The tests involved the application of EDTA to complex with copper sulfate, the addition of oxine to lead nitrate, ozone to treat sodium cyanide, calcium peroxide to control formaldehyde, and the use of calcium sulfite to reduce chlorine.

The experiments were primarily conducted in water-filled glass tanks so that a number of factors were considered, including:

- method of use
- type of spill for which use intended
- "normal" field conditions
- duration of treatment
- recovery of contaminants - if practical.

A typical experimental approach was as follows:

Step 1 - Prepare water to simulate a field station.

- Certain cations and anions were added to create a "typical" hardness and alkalinity water.
- Temperature control produced a "normal" field situation, where necessary.
- Dimensions of container were dependent upon spill situation and volume requirements for analysis.
- A sample was taken as a control.

Step 2 - Add contaminant and mix in accordance with type of spill under review.

Step 3 - Carry out the treatment reaction.

Step 4 - Carry out initial analysis for contaminant added to assess immediate effectiveness of treatment.

Step 5 - Remove additional samples over time for analysis of
- possible by-products
- unreacted agent (if necessary)
- original contaminant to assess stability of complex formed.

NOTE: UV light and aeration were applied to enhance possible breakdown.

Most of the analyses were carried out using:

- Atomic Absorption Spectrophotometry for metals
- Gas Chromatography for organics.

Other water analyses were undertaken to characterize the water before and after treatment, i.e. conductivity, pH, total solids, total organic carbon, major anions and cations, etc. If the system or agent under review involved the treatment of contaminated soil, the use of percolation columns was considered.

In some cases, the analytical protocol was tailored specifically to the treatment under review. For example, in the case of treating a copper spill with EDTA, a soluble complex is formed. Resulting samples collected, when analyzed by traditional atomic absorption spectrophotometry methods, will show no apparent reduction in free copper since the copper-EDTA complex will be in solution along with the free copper. To accommodate this problem, a colourimetric procedure (neocuproine method) was used to assay free copper (APHA 1980).

An exact list of tests and analytical procedures will appear in the final report.

Task 4 Data Analysis, Reporting

At the time of writing of this paper, analysis of data had begun on a preliminary basis only. A comprehensive report will ultimately be prepared and submitted to EETD prior to March 31, 1986 describing the study findings.

Acknowledgements

This project was conducted under the direction of Mr. M.F. Fingas of the Environmental Emergencies Technology Division of the Environmental Protection Service, who provided valuable insight into current methodologies in chemical spill control. Dr. C. Van Netten of the University of British Columbia contributed to the study team's understanding of the reactivity of reagents and the chemical pathways which these might take when applied to toxic substances.

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CONTINUING DEVELOPMENT OF A VEHICLE-PORTABLE ANALYTICAL SYSTEM

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INTRODUCTION

Following a major chemical spill incident, spill responders should be implementing effective cautionary measures which deal with the preservation of human life and health, with the minimization of property damage and with the protection of the natural environment, and corrective response measures which deal with the utilization of collection systems, and chemical and physical treatment systems. In order to choose the most appropriate of these response measures for the specific spill incident it is necessary to have a knowledge of the chemical, physical, toxicological and environmental properties of the substances involved, and to have analytical systems which are capable of rapid, on-site determinations of the identity and of the concentrations in air, water and soil in the vicinity of the spill site.

BACKGROUND

For the last five years, Environment Canada has had an on-going project to develop such analytical systems. Initially the project began with a worldwide survey of instruments, equipment and techniques, as well as a Canada-wide search of the 150 most frequently spilled chemicals (1). At the conclusion of the survey, it was discovered that systems directly usable for spill response did not exist. However, a number of systems were identified which had the possibility of being evaluated and developed for this purpose.

The existing capability was divided into five categories, based on criteria of portability, accuracy, and complexity. These are:

- pocket-portable equipment based on reagent colour changes;
- person-portable detectors based on electronic meter detectors;
- vehicle-portable instruments normally found in a fixed laboratory combined with micro-computer technology to simplify operation;
- mobile laboratories, towable on good roads; and
- fixed laboratories.

VEHICLE-PORTABLE ANALYTICAL CONCEPT

The vehicle-portable analytical system was considered to be the most appropriate category for quantitatively and qualitatively monitoring highly toxic substances (individually and in mixtures) in all three environmental compartments following a spill (2, 3).

The vehicle-portable analytical concept involves instrumentation which would normally be found in a fixed laboratory and operated by a trained operator. The instrumentation would be located in a van, containing some support equipment (e.g. glassware, columns, gas cylinders, chemicals, etc...), electrical power (e.g. fans, air conditioner), protective equipment for the operators, and the pocket-portable and person-portable analytical systems. The equipment would make use of available microprocessor technology and the associated software to make it possible for a person without extensive training in chemistry or analytical instrumentation methodology and working under emergency conditions to operate the instrument and obtain results useful for spill response. This would be accomplished by providing a user-friendly interface during the data acquisition and analysis, and by performing certain control and analytical tasks normally done by an operator with chemical training.

DEVELOPMENT OF VEHICLE-PORTABLE ANALYTICAL SYSTEM

After having developed the vehicle-portable analytical system concepts, Environment Canada proceeded to assess the potential application of commercially available analytical instrumentation. A Perkin-Elmer Sigma 2000 Gas Chromatograph (GC) with a IBM personal computer (disk drive and a hard disk), integrator and printer was selected by EETD for initial development as a vehicle-portable analytical system. The Sigma 2000 GC was equipped with a photoionization detector (PID), a flame ionization detector (FID) and a electron capture detector (ECD). The gas chromatograph was also equipped with a 2 meter 3% SP-2100/100-120 Supelcoport packed column, a 30 meter DB-5 Megabore column and both standard flash evaporation and head-space sampling options. The gas chromatograph oven was temperature programmed from 50°C to 220°C at a rate of 10°/min. The FID is a universal detector for organic compounds and the PID is more selective for organic compounds and can also respond to several inorganic compounds. Since the PID is essentially a non-destructive detector, the effluent from this detector is directed to the FID, without splitting the stream across two detectors. The PID and FID detectors complement the person-portable air monitoring detector systems currently being used by Environment Canada (e.g. HNU and OVA) and should be suitable for most field applications. Also, a ECD has been added to the GC for the analysis of polychlorinated biphenyls. This detector can be switched on when the sample is expected to contain PCB's or other halogenated compounds to which the ECD responds. The head-space sampler can be used for direct analysis of organic priority chemicals in water, soil and sorbents, eliminating the need for extensive sampling preparation (e.g. extraction, clean-up, concentrating).

The Sigma 2000 GC has been interfaced to a IBM PC/XT micro-computer with keyboard, Hercules Graphic card, AST Superdrive Card and LIBMIB Labnet Monochrome Monitor, Labnet Communication System and Spectra Physics 4270 Computing Integrator, which is capable of real-time data acquisition and post-run data manipulation. The computer can handle data from two detectors simultaneously.

Presently, the existing software is being further modified and developed for user-friendly control of data acquisition, storage and preliminary processing. Preliminary processing consists of searching the data for peaks, computing their areas, retention times and relative retention times when compared to a standard, calculating concentrations present by knowing instrument response factors and calibration studies for each substance and finally reporting this information. Software is also being developed for a library-based system to make the analysis and identification of samples possible under the vehicle-portable analytical system conditions. This will involve producing a library of retention times for specific pure compounds, alone, and for specific mixtures (e.g. fingerprinting of Arochlors or crude oils), calibration results and response factors for substances on the the priority chemical list. In order to correct the effects of instrumentation and column factors, the data will be stored as values relative to a standard sample run on the same day. The operator at a spill site will also have to run a standard as well as the field samples. The software will then compare the field value to those in the library and report compounds of the closest fits for identification purposes (the most probable substances) and amounts present. In addition to the retention time, an identification criterion will be the relative response of the PID, FID and ECD to a given substance (individually or in a mixture) and the relative responses from two of the previously mentioned columns. This system will be able to identify compounds in the following situations:

1. when only one pure compound is spilled (e.g. hexane);
2. when a mixture of several pure compounds is spilled (e.g. hexane, benzene, toluene and methanol);
3. when a mixture of many compounds (e.g. crude oils and PCBs which upon analysis by GC give a characteristic trace) is spilled;
4. when a pure compound is spilled with a mixture of many compounds (e.g. methanol and PCBs); and
5. when two mixtures of many compounds are spilled (e.g. crude oil with PCBs).

These modifications and development for user-friendly control of data acquisition, storage and preliminary processing and for a library-based system to make the analysis and identification of samples possible under the vehicle-portable analytical system conditions will be completed soon.

Calibrations for 50 compounds from the priority list will be completed for all three media in the near future. These compounds are listed in Table 1. It is believed that this system can be programmed for several hundred compounds.

Currently, the system is being installed into a 1986 compact Ford cargo van. The van has a load capacity of 4000 lb. and the dimensions of the cargo space are 80" (height) x 80" (width) x 148" (length). An air conditioner, generator, line regulator, propane heater and fan are mounted in the van. An air filtration and pressurization system, as well as sampling devices, are also included. Vibration/shock mounts are provided for all instrumentation. Benches, cabinets and cupboards are being installed. Figure 1 is a schematic diagram of the layout of the van.

Following completion of the installation and calibration for 50 compounds in all three media, the vehicle-portable analytical system will be field tested. We hope to do this later this year.

The developments to date have shown that a vehicle-portable analytical system is possible and useful for spill incidents. New technology will provide capability to monitor more compounds and also to decrease the size and weight of the system. With the concurrent decrease in price, more response organizations can be equipped in future years for quantitatively and qualitatively monitoring highly toxic substances. This will allow spill responders to choose the most appropriate cautionary and corrective response measures for that specific spill incident.

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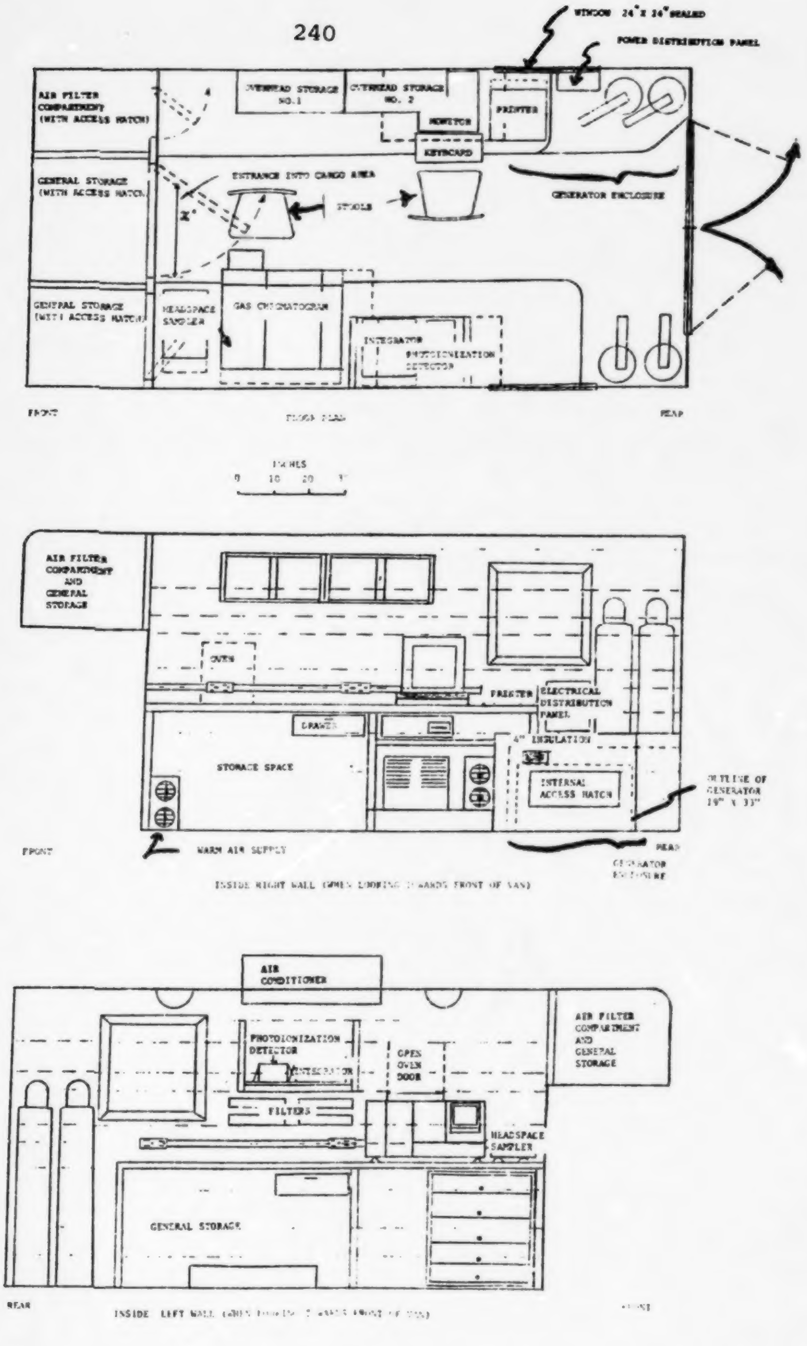
WINDOW 24" X 24" SEALED
POWER DISTRIBUTION PANEL
AIR FILTER COMPARTMENT (WITH ACCESS HATCH)
OVERHEAD STORAGE NO. 1
OVERHEAD STORAGE NO. 2
MONITOR
PRINTER
KEYBOARD
GENERAL STORAGE (WITH ACCESS HATCH)
ENTRANCE INTO CARGO AREA
STOOLS
GENERATOR ENCLOSURE
GENERAL STORAGE (WITH ACCESS HATCH)
HEADSPACE SAMPLER
GAS CHROMATOGRAM
INTEGRATOR
PHOTOIONIZATION DETECTOR
FRONT
FLOOR PLAN
REAR
INCHES
0
10
20
30
AIR FILTER COMPARTMENT AND GENERAL STORAGE
OVEN
PRINTER
ELECTRICAL DISTRIBUTION PANEL
DRAWER
4" INSULATION
STORAGE SPACE
INTERNAL ACCESS HATCH
OUTLINE OF GENERATOR 19" X 33"
FRONT
WARM AIR SUPPLY
REAR
GENERATOR ENCLOSURE
INSIDE RIGHT WALL (WHEN LOOKING TOWARDS FRONT OF VAN)
AIR CONDITIONER
PHOTOIONIZATION DETECTOR
INTEGRATOR
OPEN OVEN DOOR
AIR FILTER COMPARTMENT AND GENERAL STORAGE
FILTERS
HEADSPACE SAMPLER
GENERAL STORAGE
REAR
INSIDE LEFT WALL (WHEN LOOKING TOWARDS FRONT OF VAN)
FRONT

Figure 1: Schematic diagram of the layout of the van.

TABLE 1

Compounds from the priority list which will have data stored in the Vehicle-Portable Analytical System in the near future.

Acetic Anhydride
Acetone
Acetylene
Aminocarb Pesticide (Matacil)
Ammonia
Benzene
Butanols
Butylene
Butyraldehydes
Carbon Disulfide
Chloroform
Cyclohexane
Dichlorobenzene
Ethanol
Ethylbenzene
Ethylene
Crude Oil
Ethylene Dibromide
Ethylene Dichloride
Ethylene Glycol
2-Ethylhexanol
Fluorochloromethanes
Formaldehyde
n-Hexane
Hydrogen Sulfide
Isopropanol
Isopropylbenzene
Malathion
Methanol
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methylene Chloride
Naphtha
Natural Gas
Nonyl Phenol
Pentachlorophenols
Perchloroethylene
Polychlorinated Biphenyls (e.g. Arochlors 1016,1242,1248,1258,1260)
Propylene
Styrene
Terphenyls
Toluene
Triallate Pesticide
Trichlorfon Pesticide
Trifluralin Pesticide
Trinitrotoluene
Turpentine
Vinyl Acetate
Vinyl Chloride
Xylenes

SUMMARY OF U.S. ENVIRONMENTAL PROTECTION AGENCY, OFFICE OF EMERGENCY AND REMEDIAL RESPONSE'S, FIELD STANDARD OPERATING PROCEDURES, (FSOP'S).

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The U.S. Environmental Protection Agency's, Environmental Response Team, (ERT) was established in October 1978 to provide technical assistance to On-Scene Coordinators (OSC's), Regional Response Teams (RRT's), EPA Headquarters and Regional Offices, as well as other government agencies in the area of emergency environmental issues such as chemical spills and uncontrolled hazardous waste sites.

The Field Standard Operating Procedures (FSOP's) have been derived by reorganizing the U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C., "Standard Operating Safety Guides", November 1984. These documents provide field procedures for response personnel in a format more appropriate for field use at hazardous materials response activities than the Standard Operating Safety Guides. The objectives of the FSOP's are to provide response personnel with "Cook Book" procedures to minimize the risk of exposure to hazardous substances while field personnel are performing the document's subject activity.

At present, the following FSOP's have been printed and distributed to the appropriate Agency personnel:

FSOP No. 4 - Site Entry
FSOP No. 6 - Work Zones
FSOP No. 7 - Decontamination of Response Personnel
FSOP No. 8 - Air Surveillance
FSOP No. 9 - Site Safety Plan.

FSOP's No. 1 through No. 9 consist of the same subject matter as Parts 1 through 9 in the "Standard Operating Safety Guides", November 1984. Any additional FSOP material will start with FSOP No. 10. For example, FSOP No. 10 will address Drum Opening.

The purpose of this paper is to briefly describe the contents of each FSOP printed to date. The author hopes this summary will assist other hazardous material response personnel in evaluating the subject FSOP's, as well as other types of field response activities.

Field Standard Operating Procedures No. 4 - Site Entry

This thirty-five page document contains the major topics regarding site entry and is intended to provide site entry procedures that field response personnel can use to minimize the risk of exposure. The following are some of the major highlights of this FSOP:

1. Section-II - Personnel Protective Equipment
   This area addresses the OERR levels of protection, equipment, and selection criteria.

2. Section IV - Flow Charts for Site Entry
   This portion demonstrates entrance of personnel and equipment into the Exclusion Zone.

3. Section V & VI - Procedures for Donning and Doffing Protective Equipment
These sections address the type of equipment needed, as well as the step-by-step sequence for donning and doffing Levels A, B, and C protective equipment.

4. Section VII - Summary of Field Equipment
This area furnishes a brief description of organic gases/vapors, inorganic gases/vapors, radiation, oxygen deficiency, combustible gases, and visual observations. Also, it addresses the type of instruments used for monitoring, as well as some of the ambient levels of organic gases/vapors.

5. Section VIII - SCBA Checkout Procedures
This portion furnishes a step-by-step check-out procedure for various types of self-contained breathing apparatus.

Field Standard Operating Procedures No. 6 - Work Zones

This nineteen page document contains the major topics dealing with work zones and is intended to provide work zone establishing procedures that field response personnel can use to minimize the risk of exposure. The following are some of the major highlights of this FSOP:

1. Section II - Work Zones
This area defines and describes the following terms: Exclusion Zone and sub-areas within the Exclusion Zone, Contamination Reduction Zone, Support Zone, area dimensions, and monitoring/sampling.

2. Section III - Methodology for Selection of Work Zone Locations
This section furnishes a step-by-step sequential listing of the methodologies for establishing site specific work zones. For example, this document states that the first step in establishing work zones is a visual survey. Basically, there are two major factors to observe during the visual survey:

a. Determination of drainage, leachate, and/or location of spilled material.
b. Physical and topographical features of the site.

3. Section VI - Maximum/Minimum FSOP Requirements for Selection of Work Zones
This portion gives a sequential listing of the operating procedures necessary to understand and establish work place exposure potential based on minimum and maximum total gas/vapor concentrations. For example, the 1000 ppm above background (total gas/vapor concentrations) maximum concentration for Level A work zone is explained as follows: The 1000 ppm concentration above background is not meant to be rigidly followed. It is provided as a warning flag to alert site personnel of the need to further evaluate the existing situation.

The Level A protective clothing provides protection against concentrations in air greater than 1000 ppm for most substances; however, an operational restriction of 1000 ppm is established to:

a. Evaluate the need to enter environments with unknown concentrations greater than 1000 ppm.

b. Identify the specific constituents contributing to the total concentration and their associated toxic properties.
c. Determine, more precisely, concentrations of constituents.
d. Evaluate the calibration and/or sensitivity error associated with the instrument(s).
e. Evaluate instrument sensitivity to wind velocity, humidity, temperature, etc.

4. Section VII - Air Monitoring
This section summarizes the air monitoring philosophy, refers to FSOP No. 8 - Air Surveillance, and identifies five general site locations for air sampling.

Field Standard Operating Procedure No. 7 - Decontamination of Response Personnel

This thirty page document contains the major topics dealing with the decontamination of on-site personnel. It is intended to provide decontamination procedures that field response personnel can use to minimize the risk of exposure to hazardous substances. The following are some of the major highlights of this FSOP:

1. Section II - Flow Charts for Decontamination Layouts
This portion furnishes maximum and minimum decontamination flow sheet layouts for protective clothing Levels A, B, and C.

2. Section IV - Decontamination Procedures
This section provides a step-by-step sequential listing of maximum and minimum measures involved in implementing a site specific decontamination procedure for Levels A, B, and C protective clothing.

3. Section V - Decontamination Equipment
This section provides a station-by-station listing of the various logistical and support equipment needed for both the minimum and maximum decontamination conditions for Levels A, B, and C protective clothing.

Field Standard Operating Procedure No. 8 - Air Surveillance

This twenty-four page document contains the major topics dealing with air surveillance at hazardous material response activities. The intent of this FSOP is to provide air surveillance procedures that field response personnel can use to minimize the risk of exposure to hazardous substances. The following are some of the major highlights of this FSOP:

1. Section II - Equipment
This section addresses not only the type of collection and sampling equipment used for organic gas/vapor monitoring, but it also addresses the types of hand-held, real-time field instruments.

2. Section IV - Procedures for On-Site Air Monitoring
This portion provides a step-by-step sequential listing of the necessary procedures to follow in hazardous waste response activities air sampling. The procedures address not only the equipment and the sampling sequence, but they address sample volumes and flow rates.

3. Section VI - Procedures for Air Surveillance in Well Headspace

This area provides a step-by-step sequential listing of the appropriate procedures for collecting an air sample within a well headspace by two different methods (direct pull technique and water sample headspace).

Field Standard Operating Procedure No. 9 - Site Safety Plan

This twenty-six page document contains the major topics dealing with the development of a site specific safety plan. It is intended to provide the appropriate information to develop a site safety plan that field response personnel can use to minimize the risk of exposure to hazardous substances. The following are some of the major highlights of this FSOP:

1. Section II - General Requirements

This portion furnishes a sequential listing of factors which are a must for a hazardous material response activity.

2. Section III - Plan Development

This section identifies three major items which must be addressed in a site safety plan; routine operations, contingency planning for on-site emergency, and incident-specific variables. To develop the plan, as much background information as possible should be obtained about the incident. After the background information has been obtained, the FSOP assists to identify routine operations which must be addressed in a site safety plan. For example, the plan must describe the known hazards and risks, key personnel and alternates, designated levels of protection, designated work areas, etc. This section also addresses key factors to be considered for a plan that covers the on-site emergencies.

3. Section V - Sample Safety Plans and Operating Codes

This area furnishes two examples of generic site safety plans. In addition, it furnishes an example of emergency operation codes for real-time monitors and ERT's employee's response safety check-off sheet.

CONCLUSION

The author hopes other field response individuals find this summary useful. The procedures mentioned are currently being used by ERT and others at both hazardous waste sites and chemical spill responses. The procedures are continuously being updated and modified for each specific response.

ACKNOWLEDGMENT

The author expresses his appreciation to all members of the U.S. EPA's Environmental Response Team, U.S. EPA, ERT's Technical Assistance Team - Edison, NJ, and U.S. EPA, EERU Contractor, Edison, NJ for their many contributions and constant updating of our procedures.

DISCLAIMER

The mention of trade names or commercial products in this paper or the FSOP's is for illustration purposes and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Contents of this paper do not necessarily reflect the views and policies of the Environmental Protection Agency.

The Utility of Fully Encapcapsulating Chemical Protective Suits in U.S. Coast Guard Hazardous Chemical Response

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INTRODUCTION:

The development of a hazardous chemical personnel protective suit for use in the field involves a carefully balanced tradeoff between the results gained in the laboratory, operational requirements, psychological needs, and economic considerations. In 1980 the United States Coast Guard began the development of a total encapsulating protective suit for personnel that would meet Coast Guard requirements and offer superior chemical protection. Production of this suit has begun and its deployment will begin in June of this year. The rationale for fully encapsulating protective clothing and the Coast Guard's new suit is the subject of this paper

The United States Coast Guard is the federal on-scene commander for hazardous chemical spills into or near the navigable waters of the United States. To be able to safely execute this responsibility the Coast Guard must provide its chemical response personnel with appropriate protective clothing. Chemical protective clothing ranges from coveralls with gloves and boots to fully encapsulating suits. Encapsulating suits offer the highest level of protection. These suits in combination with breathing apparatus form an ensemble which protect the wearer from chemical inhalation and skin absorbtion hazards. This level of protection is used when the chemical involved is dermally toxic or when a high degree of uncertainty exists as to what chemical is involved. The Coast Guard uses its CHRIS (Chemical Hazard Response Information System) to determine the toxicity of spilled chemicals. Requirements for using encapsulating suits for particular chemicals were established in a study done by Mine Safety Appliances Company (MSA) for the Coast Guard. (1)

CLASSIFICATION OF ENCAPSULATING SUITS

What is a fully encapsulating hazardous chemical protective suit? Unfortunately, such a suit is not as easily defined as one may assume. The American Society For Testing and Materials (ASTM) currently defines it as a garment that fully encapsulates the user and his or her air supply; this definition would exclude airline suits from the classification of full encapsulation. The

Swedish regulations require that the air supply be worn outside the suit and a number of manufacturers market fully encapsulating suits that have large, unregulated, unprotected passages through the protective membranes. At least three distinct types of fully encapsulating suits are in common usage. For the purposes of this paper they shall be referred to as: Type 1 encapsulating suits that completely enclose the wearer and the air supply (ASTM definition); Type 2 encapsulating suits in which the air supply is worn externally and the breathing apparatus mask completes the encapsulation; Type 3 encapsulating suits that fully encapsulate the wearer but rely on an airline respiration system with or without an emergency self-contained breathing apparatus (SCBA) [Figure 1 pictures these types]. There are additional variations of encapsulating suits which cannot be classified according to these types. A comparison of each of these encapsulating suit types follows with the rational the Coast Guard uses for its chemical response operations.

TYPE 1 ENCAPSULATING SUITS

Features of the Type 1 Total Encapsulating Suit include full encapsulation of the user and the air supply in a protective membrane. This requires integral (but not necessarily permanently attached) gloves and boots; positive air pressure inside the suit maintained by exhaust air from the SCBA and suit exhaust valves. The rational behind the Type 1 fully encapsulating suit is that the suit user should be encased in a material to which the effects of the challenge chemical can be determined or at least predicted. Alternatively, if the user was to have his air supply outside the protective membrane the interaction possibilities of challange chemicals would increase dramatically as with the many different elastomers and materials such as natural rubber, silicone, neoprene present in many commercial breathing apparatuses. Note that Figure 2 shows a representative self contained breathing apparatus and common materials for the construction of its components.

The postulate that limited chemical exposure implies relatively little risk was explored by the Coast Guard R&D Center. The standard ASTM F739 Standard Test Method For Measurement of Permeation Resistance by Liquid Chemicals was modified to allow comparison of continuous chemical material contact, varied frequencies of contact, simulating splashes, and constant vapor contact over a three hour period. (2) The initial hypothesis was that permeation breakthrough time should become longer with diminishing molecular contact. Indeed this behavior was noted for many material/chemical combinations. However, in a significant number of combinations, permeation breakthrough times between tests with constant liquid contact and intermittant contact were similar. It appears that the mere wetting of the material's surface may be sufficient to cause permeation in some material/chemical combinations. Table 1 shows some of these results by representative materials and chemicals. Thus unless the wetting effect of the challange chemical was known for each material that could be exposed, a continuous chemical contact breakthough time would have to be used to assure the safety of the suit wearer.

In addition, matrix contamination, the phenomenon that occurs when a chemical or mixture permeates into a polymer substructure and resides there after decontamination, is another serious concern for external materials. This type of contamination warrants concern for extended use or reuse of polymers exposed to chemicals because such contamination may alter the material's physical and chemical resistance properties. This is particularily important in considering the materials involved in respiratory apparatus such as the diaphragm. In a test performed by the Coast Guard R&D Center, samples of viton/chlorobutyl laminate were exposed to ethyl acrylate.(3) Breakthrough times of 15-30 minutes were recorded. Attempts then were made to decontaminate these samples using solvent washing with freon and vacuum dessication. Even after six freon washings, the odor of the ethyl acrylate was still detectable on the samples. Subsequent permeation testing of these samples revealed a 5-10 minute decrease in the measured breakthrough times. Even the most promising decontamination methods are not likely to remove matrix contamination. This is another important reason why only materials intended to be chemical "barrier" materials should be on the external parts of a protective ensemble.

Arguments in support of wearing the breathing supply on the outside of the suit (4) are, first, that it allows for easy replacement of the air bottle and, second, that a injured responder can be better helped because his air supply is accessable and therefore his immediate evacuation is not necessary. These arguments do not always hold true, however. Lightweight composite air bottles provide up to a one hour supply of air which greatly reduces the need to change air bottles. Furthermore, the wisdom of sending a person who has been working at a spill incident in an encapsulating suit for an hour back in with only an air supply change must be questioned for the following reasons. An encapsulating suit, the air supply, communication equipment and boots not including any tools or detection equipment which the user must carry can weigh more than sixty pounds. Work that is done while in "gas protective clothing in the chemical industry could be classified as very heavy work irrespective of age".(5) The mean heart rate and pulmonary ventilation rates of a man involved in work in an encapsulating suit are above that which a man can expect to work continuously.(6) Additionally, an injured user wearing an external air supply may be helped more readily than the user of an internal supply only if it is assumed that the cause of his injury does not dislodge his exposed SCBA mask and that no additional air can be supplied to the user of an internal supply without opening his suit. A protective suit with an internally worn air supply provides the user with clean air even in the event of dislodging or damage to the SCBA mask. Moreover, supplying air to an injured man whose air supply is exhausted in a suit with an internal air supply is easily accomplished with a tool recently designed by the Coast Guard.(Figure 3) An additional benefit of an internal air supply is that a suit user who experiences a sudden loss of air flow has the option of dislodging his SCBA mask and breathing off the clean air supply in the suit. Using air trapped in the suit (approximately 220 liters) will provide six to eight minutes of breathable air.

Fully encapsulating protective suits should maintain a slight positive (2-4 iwp) internal pressure of air. This positive pressure helps to minimize the effects of pin holes that can develop while the suit is being worn. During manned stress testing performed for the Coast Guard between November and January 1984-1985 prototypes of four types of suits (butyl, viton/chlorobutyl, chlorinated polyethylene, and a reinforced chlorinated polyethylene) were tested under controlled conditions. After each test the suits were inspected for damage. In twenty nine out of thirty one inspections the suits required repair. However, this does not mean that a higher pressure would be more benefical. Too high a pressure would make movement exceedingly difficult. Nonetheless, the feature of positive pressure in a Type 1 encapsulating suit provides additional integrity over a Type 2 suit.

COOLING REQUIREMENTS

The need for cooling in a Type 1 suit varies according to the weather conditions in which the suit will be worn. In a recent study subjects wearing encapsulating suits went through a senario that resembled a chemical response. The ambient temperature was two degrees centigradeC. After approximately 37 minutes a mean weight loss of 0.3 kg was recorded and was attributed to mostly sweat.(5) Obviously a greater ambeint temperature would produce greater thermal stress in a suit user. The mean heart rate recorded during that study was 147. A correlation can be made between a man's heart rate and a man's production of heat.(7) A heart rate of 147 indicates a heat production of approximately 2400 BTUH. In addition, radiant energy from the sun will provide additional excess heat that must be contended with. Although commercially available cooling vests designed to be worn within a type 1 or 2 suit have an advertised cooling capacity of approximately 1400 BTUH, the effectiveness of these garments actually cooling a man's core temperature has not been tested scientifically. A Coast Guard engineering anaylsis of a recently developed full body cooling garment which was designed by one of the largest producers of cooling garments indicates the actual potential cooling may only be approximately 500 BTUH. In addition to the question of how much a cooling garment is capable of cooling is the question of how a cooling garment works to cool a person. Since the body normally looses heat through three methods: radiation, conduction and evaporation (heat loss 60%, 15%, and 22% respectively) (8) and since the suit acts as an insulator slowing heat transfer down and trapping hot moist air against the suit user, it is possible the relief cooling garment users have noted is more psychological than physiological.

TYPE 3 ENCAPSULATING SUITS

Type 3 encapsulating suits have many advantages if they are equipped with chemically resistant air lines and the the situation allows their use. The obvious limitation of a Type 3 suit is the umbilical air line. The air line restricts movement, its length according to NIOSH is limited to 300 feet, and these hoses are typically constructed of neoprene rubber which usually has much lower chemical resistance than the primary suit material. The advantages of an airline system are: potentially unlimited air supply, effective cooling possible because cool air can be pumped into the suit, hard wire communications uneffected by radio noise can be maintained, and the user is not required to carry as much weight as a user of a Type 1 or 2 encapsulating suit. The Coast Guard's need for flexibility in responding to all types of chemical spills precludes its use of Type 3 encapsulating suits. On the other hand the U.S. Army has made extensive use of these suits in the inspection of stores inside of bunkers. In that situation the distance between the hot zone and the uncontaminated area is short.

COAST GUARD'S TEFLON/NOMEX TYPE 1 ENCAPSULATING SUIT

The U.S. Coast Guard will deploy a newly developed Type 1 fully encapsulating protective suit this spring. The suit is constructed of a teflon/nomex fabric that provides greater chemical permeation resistance than any material we have tested to date which include: viton, chlorobutyl, chlorinated polyethylene, neoprene, fluorosilicon and others. Table 2 compares some of the permeation testing results of this teflon/nomex laminate with other more common materials.

The laminate developer and suit producer, Chemical Fabrics Corporation (Merrimack, New Hampshire), has developed a proprietary process of laminating the teflon that prevents the microfracturing that had led the National Institute of Occupational Safety and Health to question its viability as a protective clothing material.(9) Chemical Fabrics Corporation has also managed to produce their material at a cost that is comparable to a viton/chlorobutyl laminate. The material resists also heat up to 260 C and remains flexible to -32 C.

The suit is sewn and then heat sealed together so there are no exposed threads or adhesives. The visor and glove liners are teflon and the gas tight zipper is encased in a teflon cofferdam which provides the suit user with a formidable and predictable protective barrier against the challange chemicals he is entering.

CONTINUED SUIT DEVELOPMENT

Continued research and development will support the production and deployment of the Coast Guard's hazardous chemical protective suit. All materiials used in the construction of the suit will be extensively tested against approximately 400 chemicals chosen on the basis of spill frequency, toxicity, and need for encapsulation. This testing will primarily include material permeation testing, but will also involve some specialized testing to determine specific material-chemical effects. Among these effects will be further "splash" testing with the objective of finding a material or chemical parameter that allows a predetermination of material wettability, and a closer look at material matrix examination. This latter study will involve the use of radioisotope tagged chemical challenge agents to determine the extent of chemical permeation, and the effectiveness of traditional chemical decontamination methods. Other testing will encompass the entire garment, seams and other marked interfaces using a standard ASTM penetration method. Complete ensemble testing will be conducted at Lawrence Livermore National Laboratory to measure suit protection factors between encapsulating and non-encapsulating suits, and among commercial products as well.

The U.S. Coast Guard and other U.S. Government Agencies are participating in standards organizations such as the ASTM and the NFPA (National Fire Protection Association). Work in the ASTM is directed towards the development of suit and suit component testing methodology which allows reproducible testing and simulates field conditions. One subcommittee of ASTM is pursuing the development of standard chemical suit specifications that would recommend minimum suit documentation by manufacturers. This specification recommends the information that should be provided by the manufacturer, including suggested test methods for determining the performance of the entire suit and suit components. NFPA is starting to work on standards that will set performance requirements related to chemical protective clothing worn by U.S. firefighters. These same standards may generally apply to other workers involved in hazardous chemical response.

NOTE: The authors' views do not necessarily represent those of the Unites States Coast Guard.

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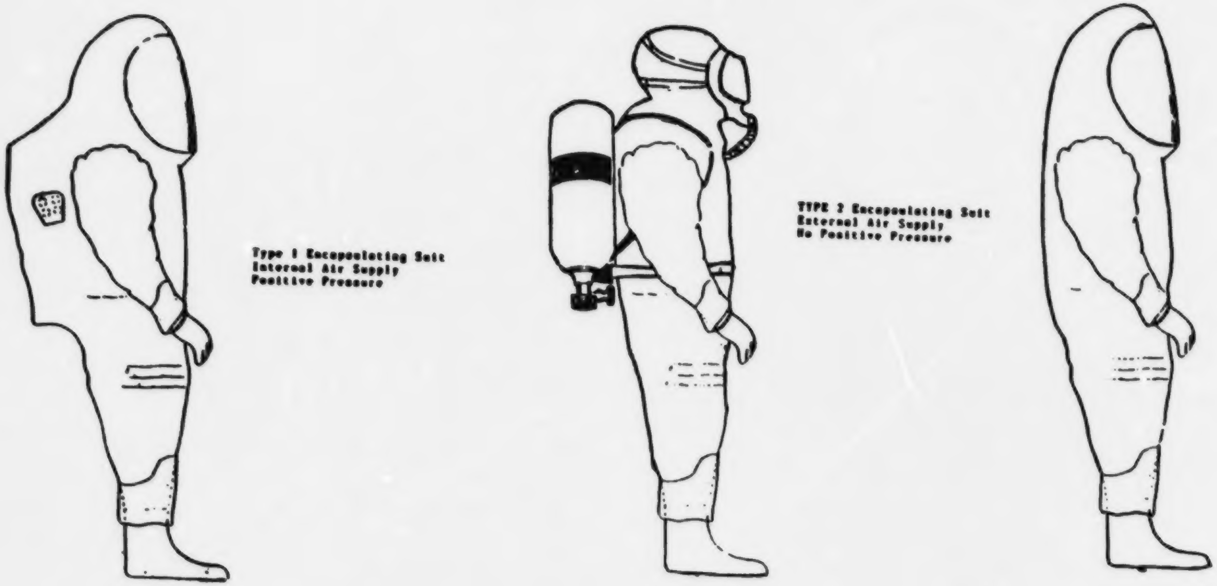


Type 1 Encapsulating Suit
Internal Air Supply
Positive Pressure

TYPE 2 Encapsulating Suit
External Air Supply
No Positive Pressure

Type 3 Encapsulating Suit
Umbilical Air Line
Positive Pressure

FIGURE 1

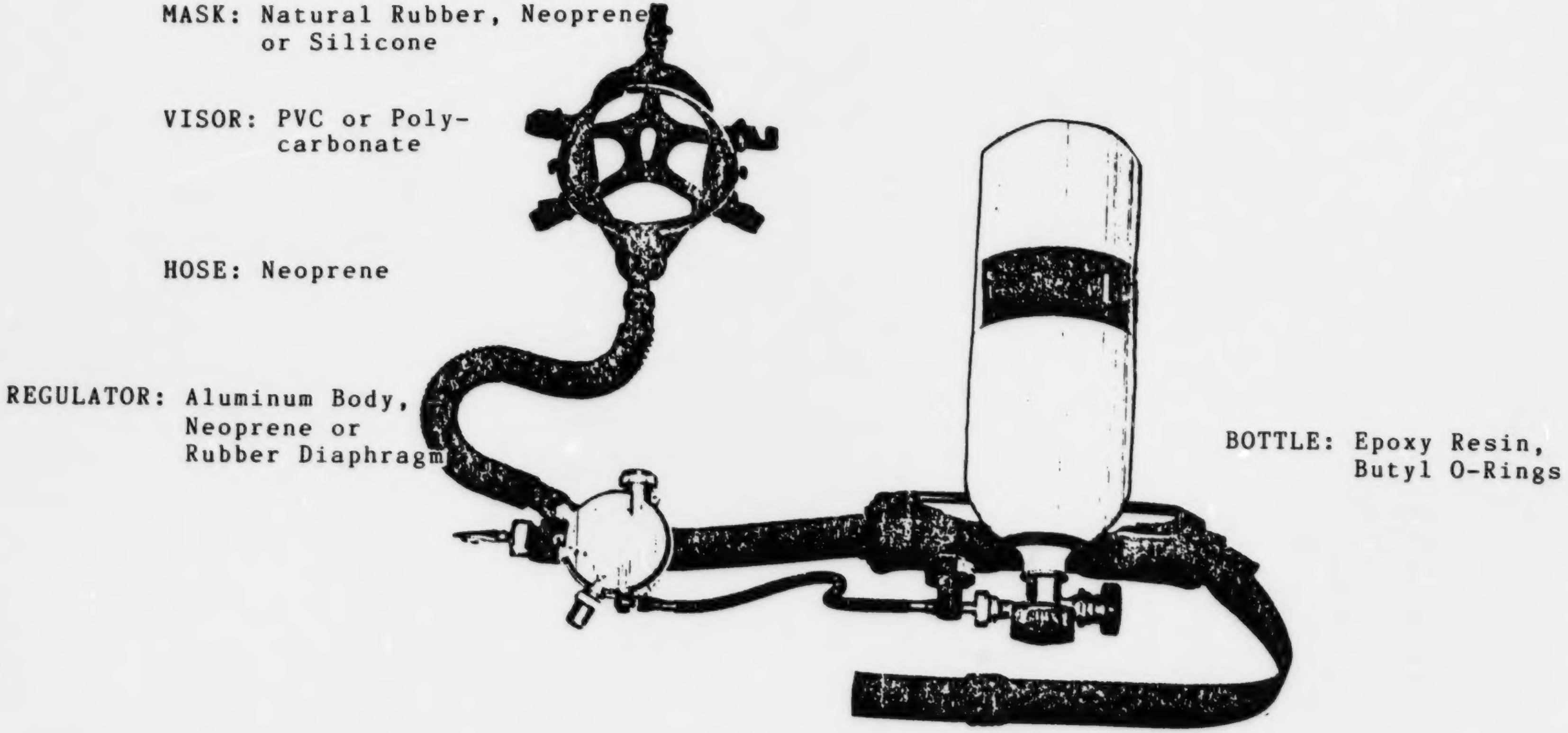

MASK: Natural Rubber, Neoprene
or Silicone
VISOR: PVC or Poly-
carbonate
HOSE: Neoprene
REGULATOR: Aluminum Body,
Neoprene or
Rubber Diaphragm
BOTTLE: Epoxy Resin,
Butyl O-Rings

FIGURE 2

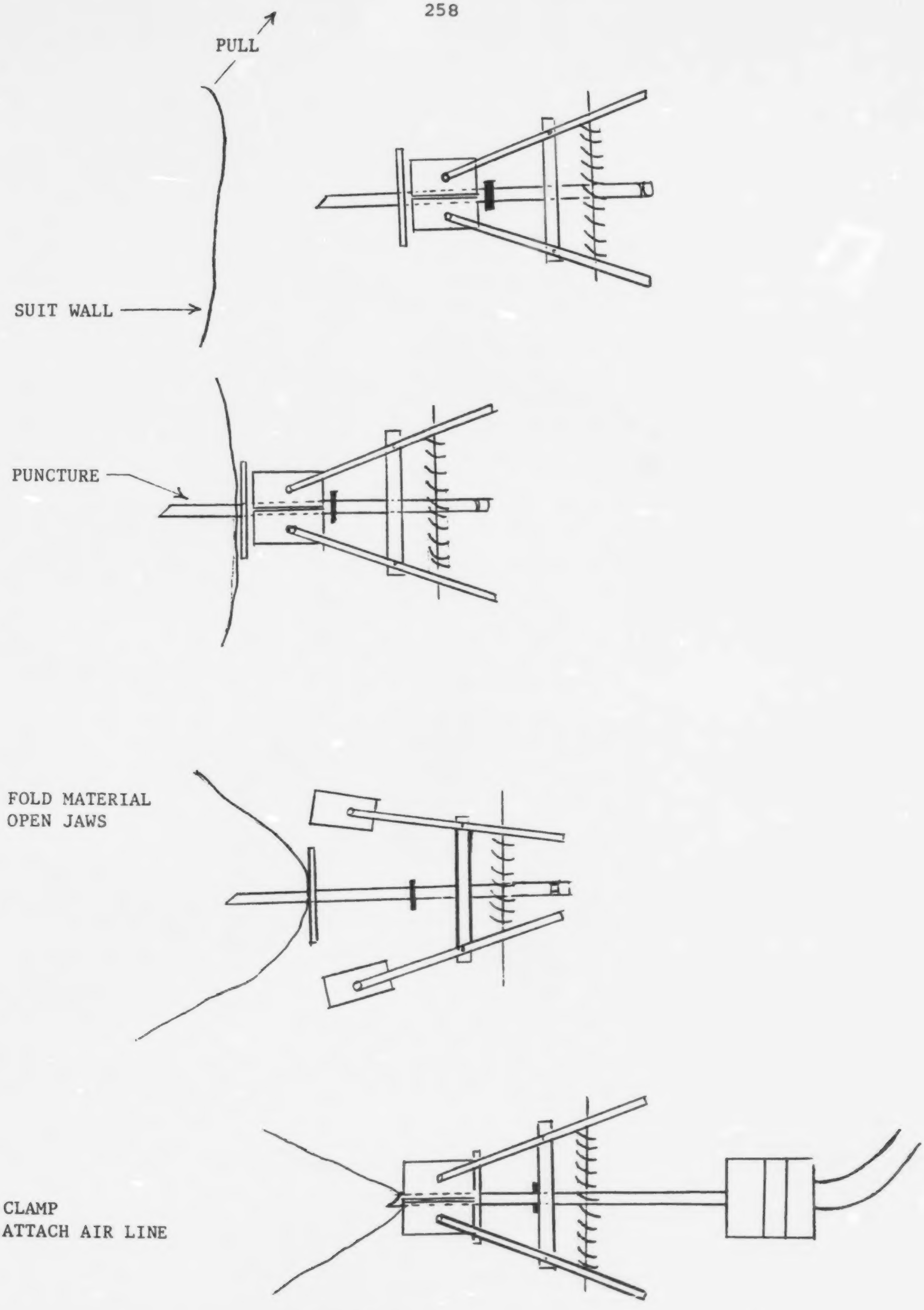
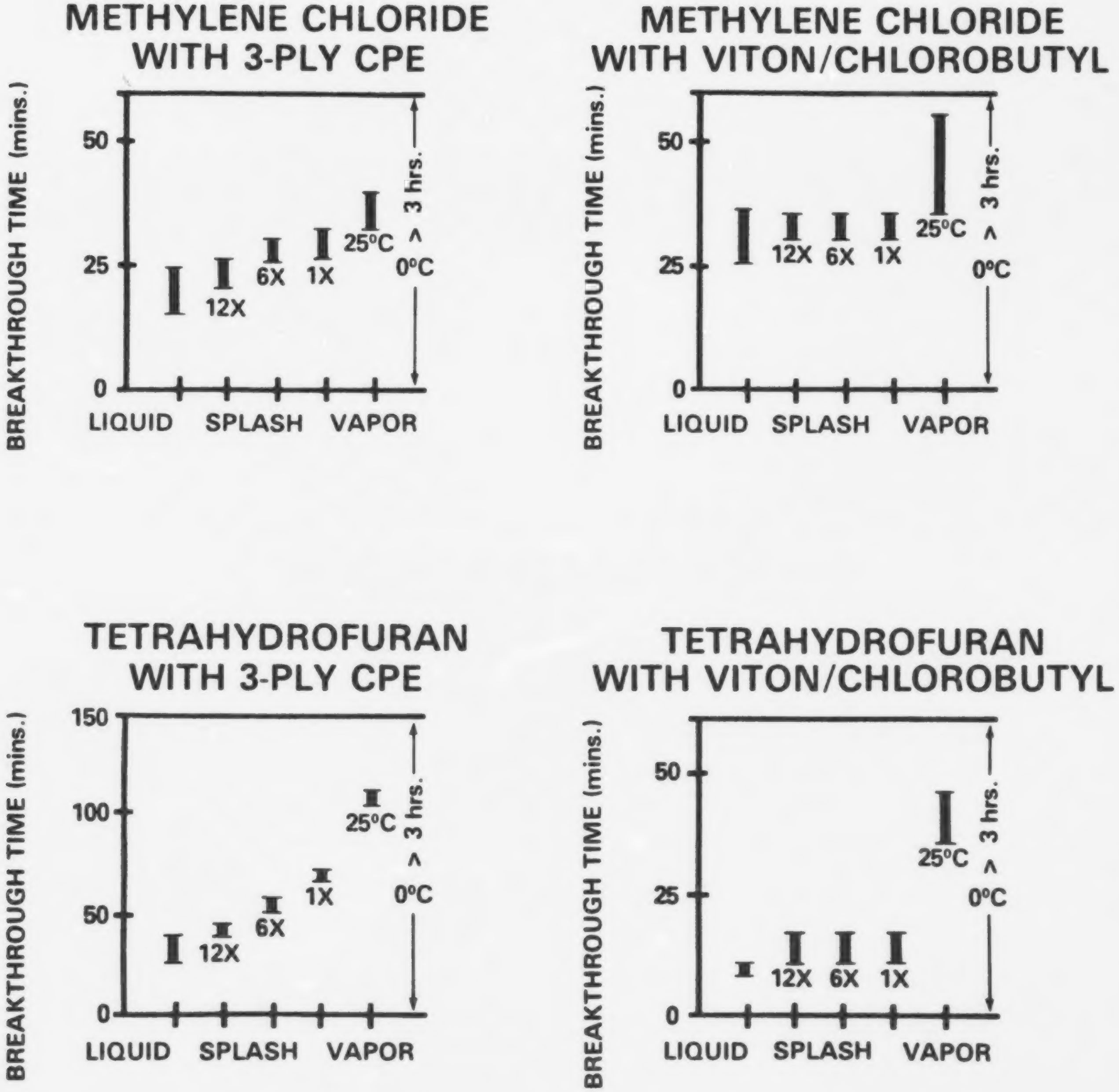

PULL
SUIT WALL
PUNCTURE
FOLD MATERIAL
OPEN JAWS
CLAMP
ATTACH AIR LINE

FIGURE 3



METHYLENE CHLORIDE WITH 3-PLY CPE

METHYLENE CHLORIDE WITH VITON/CHLOROBUTYL

TETRAHYDROFURAN WITH 3-PLY CPE

TETRAHYDROFURAN WITH VITON/CHLOROBUTYL

TABLE 1

TABLE 2

CHEMICAL COMPOUND	BREAKTHROUGH TIME (Min.)*
Acedic Acid	>480
Acetonitrile	>480
Diethylamine	>480
Diethylether	>480
Dimethyl Formamide	>480
Dimethyl Sulfoxide	>240**
Ethyl Acrylate	>480
Trichlorotriflouroethane	>480
Hexane	>480
Methanol	>480
Methyl Ethyl Ketone	>480
Nitrobenzene	>480
Oleum	>480
Sodium Hydroxide (20% w/v)	>480
Tetrahydrofuran	>480
Toluene	>480

*Testing conducted by Radian Corp. using ASTM Test Method F739, with a sensitivity of 1ppm.

** This test was conducted at the Coast Guard R&D Ctr. using ASTM Test Method F739 with a sensitivity of 1ppm.

The Coast Guard R&D Ctr. is conducting further testing using additional chemicals and higher sensitivities.

CONTINUING DEVELOPMENT OF A PERSON-PORTABLE ANALYTICAL SYSTEM

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During the last few years, a number of chemical spill incidents in Canada, involving PCBs, vinyl chloride, aromatics, etc., have once again shown the urgent need for on-site analytical systems which can detect, qualitatively and quantitatively, substances in air, water, and soil in a time period of a few hours. In most of these cases, samples were taken at the spill site, transferred to a laboratory, and then analysed. This whole process took from one to several days before qualitative and quantitative measurements became available to spill responders. However, following a chemical spill incident, rapid and reasonably accurate determinations of the spilled chemicals in air, water, and soil within the vicinity of the spill site are needed to provide effective response measures especially in situations where environmental conditions are rapidly changing. Measurements of concentrations in air are the most critical immediately after a spill incident since they are needed to make decisions on protection measures for both the spill responders and the surrounding population. Measurements of the concentrations of the spilled chemicals in surface water and soil are useful in providing information for planning clean-up operations, making decisions on protection measures for the surrounding population, and assessing environmental damage since these two media provide a pathway for the chemicals to travel beyond the immediate spill area.

Recognizing that these rapid analytical field-portable requirements were not adequately met in most spill situations, Environment Canada's Environmental Protection Service (EPS), which is responsible for developing and coordinating programs aimed at achieving technologically sound and effective response capabilities for spills of environmentally hazardous substances, initiated, in 1980, the Chemical Hazards Emergency Countermeasures Program which would develop chemical spills response capabilities (1). As part of this program, existing analytical methods and instrumentation were reviewed to determine their capability in terms of potential applicability to spill monitoring in emergency situations. Five levels were selected based on the portability, accuracy, and complexity of the existing analytical capability. The levels selected are:

Level 1: Pocket-portable detectors, usually using colourimetric methods

Level 2: Person-portable electronic detectors and colour imeter

Level 3: Vehicle-portable computer-controlled instruments with pre-developed software

Level 4: Mobile laboratories towable on good roads

Level 5: Fixed laboratories

Levels 1, 2, and 3 were considered most appropriate for spill monitoring and currently, developmental work at EPS is being applied to Levels 2 and 3. In each case, the methods are to be suitable for use by personnel who do not have extensive training in analytical chemistry or instrumentation and who are capable of working under emergency conditions. Developmental work on each of the levels is warranted since they each have unique advantages. For instance, Level 2 instrumentation is more easily transportable than Level 3 instrumentation and will most likely require less maintenance and operator training. This will permit analysis to be done directly at a remote site. However, in most cases, it will not be as accurate or as sensitive as Level 3 and the identification of the spilled substance must be known. This paper will deal solely with Level 2.

The Level 2 system consists of person-portable instruments intended for use directly at a spill site. The instruments that are presently used for air sampling are the Century Systems Corp. Model 128 Organic Vapour Analyser (OVA) and the HNU Systems Inc. Model PI-101 Photoionization Analyser (HNU).

The OVA is basically a portable flame ionization detector (FID). In operation, a continuous, metered flow of sample air is drawn into the detector chamber where organic molecules are burned in a hydrogen flame, producing positively-charged, carbon-containing ions. These ions are driven to a negatively-charged collector electrode where a current is generated which is proportional to the ion collection rate. This current is measured with a pre-amplifier, the output signal from which is further amplified and displayed on the meter situated on the hand-held probe assembly. The detector exhibits inherently high sensitivity and responds to a wide range of organic chemicals. The OVA has its own hydrogen supply tank and rechargeable battery allowing for a mininum of eight hours of continuous operation.

The HNU is basically a portable photoionization detector (PID). In operation, a continuous flow of sample air is drawn by a fan into an ionization chamber located on a hand-held probe. Photons emitted by the 10.2 eV UV source pass through a transmitting window into the ionization chamber where this radiation is absorbed by molecules having ionization potentials of approximately 10.2 eV or less. The positive ions produced are driven to a collector electrode, where a current proportional to the concentration of the sample in air is generated. This current is amplified and used to drive a meter on the readout unit. The HNU is a selective detector since chemicals having ionization potentials much greater than 10.2 eV will not be ionized and therefore will not produce an instrument response. The HNU is capable of detecting a broad range of organic compounds, as well as a few inorganic compounds. The HNU utilizes a rechargeable battery which allows for a mininum of ten hours of continuous use.

A more detailed description of these instruments are given by Lockwood and Halman (2).

These instruments are non-specific with respect to measuring a certain chemical out of a mixture of several chemicals. In combination these detectors can be used to detect a great variety of substances. They determine total vapours present at a spill site according to the response of the specific detector used. This is not a drawback for in most spill situations only one substance is involved, which is identified easily by shipping labels or waybills, and usually the concentration of that substance is far greater than that of the ambient background.

The OVA and HNU were chosen because of their abilities to provide accurate results within a few seconds although some compounds of high boiling points may require up to two minutes for readings to attain their maximum. They are simple to use and do not require much maintenance. They are adaptable for use over a wide range of climatic conditions as found in Canada, and provide detection limits below the maximum allowable limits of the hazardous substances.

Calibrations have been completed for both instruments for the bulk of gases and vapours on the Environmental Emergencies Technology Division's (EETD) Priority List of 150 substances (1). These data have been used to design transparencies which are fitted onto the units, thus providing immediate and direct readouts of the concentrations (in ppm) present with an accuracy of about ± 10 percent. The main advantages that these units have over the Level 1 system are that concentrations over three or four orders of magnitude can be measured directly and continuously. Thus, a greater number of chemicals may be monitored. These meter scale overlays have been made of hard, clear plastic and are easily fitted over the meters on the instruments. An overlay has been made for each substance for each instrument. The spill responder will only need to know what substance is involved and this information is, in the majority of cases, readily available. More detailed information on the experimental methodology and calibration data of the OVA and HNU can be found in papers written previously by the author (3,4).

A training program for spill responders who will be using this Level 2 person-portable analytical system has been set up. Training manuals have been written which give the basic chemistry background needed to understand how the detectors work, details how to operate the instruments in a step-by-step procedure, and tips on routine maintenance and troubleshooting. This program is the first major step in providing the Level 2 air-monitoring system on a large-scale basis for on-site, person-portable use. Level 2 is reaching beyond the research and development stage and into the field.

For water and soil analysis of organic and inorganic substances, the Hach Company Direct Reading Engineer's Laboratory Model DR-EL/4 (Hach Kit) was chosen as the most suitable, available unit that could be modified to satisfy the Level 2 criteria. The Hach Kit is a portable laboratory containing a colourimeter, digital titrator, pH meter, conductivity meter, basic glassware, and pre-packaged reagents. Included with the Kit is a well-written, easily-understood manual which provides detailed step-by-step procedures. This enables the Hach Kit to be used by personnel who have not received extensive training in laboratory analysis or instrumentation. The Hach Kit has been widely used for water quality analysis in laboratories and water treatment plants. With the exception of phenol, all the methods are geared to analysing inorganic substances in water.

All of the inorganic substances from the Priority List, except for hydrogen peroxide and titanium dioxide, can be detected in water using the existing methodology of the Hach Kit. The first step in the modification of the Hach Kit was to develop methods for analysing inorganic substances in soil. It has been determined that the methods used for the analysis of inorganic substances in water can be easily modified for soil samples by simply extracting the soil sample with water first and then proceeding with the method.

The next step in the modification of the Hach Kit was to find suitable methods for the analysis of organic substances from the Priority List. Initially, the 150 priority list chemicals were arranged into groups, each of which could be amenable to analysis by a single method. Of particular interest were the spot tests in which the development of a coloured product would denote the presence of a given class of compound.

The first division into groups was into organic and inorganic substances. As stated earlier, most of the inorganic substances can be analysed for by the methods listed in the Hach Kit Manual. The next division was made by separating the substances into acids and bases. Even though other methods may be found to analyse for these chemicals, pH measurements can be used as a check or as a rapid test to determine low or high concentrations.

The next step was to divide the organic compounds into classes according to functional groups. These classes were: alkanes, aromatics, aromatic alcohols, alcohols, aldehydes, acid anhydrides, ketones, oxides, acetates, amines, amides, organic halides, and other miscellaneous compounds.

Following this grouping, a literature search was undertaken, using literature sources which included published methods for quantitative analysis of water, qualitative or "spot tests" which normally are used to detect the presence or absence of a chemical, and physical-chemical properties.

For each compound listed under the functional groups the following physical-chemical information was sought: structure, physical state (liquid or solid), reaction with water or other common substances, solubility or miscibility with water or organic solvents, and density (floats or sinks in water if not soluble). This information can be useful in determining methodology. For example, solubility data can be used to determine if water samples should first be extracted with an organic solvent before adding other reagents, or, for soil samples, whether they should be extracted with water or an organic solvent.

In the literature survey, the most sought-after methods were those that would involve adding pre-measured, packaged reagents to samples (aqueous or soil extracts), allowing a coloured product to develop, and measuring the colour intensity with a colourimeter. Methods using the digital titrator were also sought. Specific, known amounts of reagents can be added to the sample to produce a colour or a change in colour. Using the titrimetric method, the same colour is produced but the varying amounts of titrant added, correspond to a range of concentrations of the sample.

Following the literature review, a preliminary evaluation of the methodologies was done to see if these analyses could theoretically be performed successfully in the field using the Level 2 criteria. This evaluation was based on the following:

A. The equipment required for the analysis must be person-portable. The Hach Kit, at present, weighs approximately 15 kilograms. This can be a considerable weight when it has to be carried a distance over rough terrain possibly in inclement or cold weather by a spill responder in protective clothing. Therefore it is necessary to have analytical methods that will not require extra glassware or instruments.

B. The analysis must be performed in a short period of time. Length of time needed for the colour to reach its highest intensity should not take longer than twenty minutes. The colour must remain stable for a reasonable period of time to allow for readings to be taken.

C. The analysis must not be affected significantly by temperature.

D. The analysis must not produce as its end-product a precipitate or a turbid solution. Any readings obtained from the colourimeter would not be accurate and even with the titrimetric methods the endpoint is difficult to determine visually with such interference. It might be possible to filter these samples to obtain a clear-coloured solution but that takes more time and extra glassware.

E. The majority of reagents used in the analysis must have a long shelf-life (>six months) so that they can be prepared ahead of time and pre-measured into little packets. Liquids will probably be dispensed by droppers or by an automatic dispensing unit. Some reagents, namely those which undergo photolysis and are quickly degraded may have to be prepared just prior to the analysis.

F. The analysis must not be affected significantly by interferences. As stated earlier, most chemical spills only involve one chemical so the task of determining interferences is mainly concerned with naturally occurring substances, namely water, humic acids, etc.

G. For safety reasons, to the spill responders, it would be preferable not to use any concentrated acids, strong bases, or carcinogenic or mutagenic compounds in the analysis.

The methods that are listed in Tables 1 and 2 are those that have met the above-mentioned criteria and have been evaluated experimentally. Our experimental evaluation has addressed the aspects of stability, interferences, sensitivity, and detection limits in deionized water and in a loamy soil. Table 1 lists the successful methods (those that have a potential of being developed for field use) and Table 2 lists the unsuccessful methods.

The work currently in progress and planned for the future, consists of the following:

1. developing methods for the collection of water and soil samples in the field,

2. continuing experimental evaluations of methods which have met the Level 2 criteria,

3. testing the methods with various types of soils,

4. performing calibration experiments for the EETD priority list chemicals,

5. converting the calibration data to a form usable by spill responders (ie. meter scale overlays for the colourimeter and a table or graph for the titrator),

6. expanding the Hach Kit Manual to include the tests for organics developed in this study which comply with the Level 2 criteria, and

7. developing a training course for spill responders on how to use the modified Hach Kit.

Table 3 presents a summary of the present and proposed capabilities for measuring spilled substances in air, water, and soil.

These existing and potential spill monitoring capabilities associated with the OVA, HNU and Hach Kit systems provide a high degree of coverage for the EETD priority list and they are expected to develop into valuable and essential components of a comprehensive chemical spill response capability.

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TABLE 1

SUCCESSFUL METHODS

CLASS	COMPOUNDS DETECTED FROM EETD PRIORITY LIST	LOWER DETECTION LIMIT		REF. SOURCE	TYPE OF TEST	REAGENTS NEEDED	COMMENTS
		Water (mg/L)	Soil (mg/kg)				
Aromatics	Benzene	300	3000	1 13	Colourimetric	Tetracyanoethylene Methylene Chloride Acetone Chloroform	Absorbance read at 440 nm except p-terphenyl read at 550 nm.
	Toluene	150	1600				
	Styrene	200	1800				
	m-Xylene	50	600				
	o-Xylene	50	200				
	p-Xylene	50	600				
	Ethylbenzene	150	1600				
	Cumene	150	2000				
	p-Terphenyl	300	4000				
Aromatics	Styrene	30	1000	2a	Titrimetric	Mercuric Acetate Methanol Potassium Hydroxide Sodium Bromide Phenolphthalein indicator, 1% in alcohol Chloroform	Colour changes to pink.
Aromatic Alcohols	Phenol	0.1	10	3	Colourimetric	Buffer solution, Hardness 1 Phenol Reagent Phenol 2 Reagent Chloroform	Absorbance (yellow) read at 460 nm.
	Cresol		5				
	Nonylphenol		200				
Alcohols	Methanol	20	3000	4 5a	Colourimetric	Potassium Permanganate Sodium Bisulfite Phosphoric Acid Sulphuric Acic Chromotropic Acid Disodium Salt	Converts methanol to formaldehyde. Absorbance (purple) read at 570 nm. In soil, brown colour results so 570 nm may not be suitable.
Alcohols	Ethylene Glycol	2	400	2b	Titrimetric	Sodium Bicarbonate Starch Chloroform Iodine Potassium Iodide Sodium Hydroxide Arsenous Oxide Sulphuric Acid Periodic Acid	Colour changes to purple-red for analysis in water and purple in soil.
	Propylene Glycol	60	2000				
Aldehydes	Formaldehyde	0.001	5	6	Colourimetric	Phenylhydrazine Hydrochloride Potassium Ferricyanide Sodium Hydroxide Isopropanol	Absorbance (orange) read at 535 nm.
	n-Butyraldehyde	1	100				
	iso-Butyraldehyde	1	300				
Aldehydes	Formaldehyde	1	40	2c	Colourimetric	Methanol Pyridine Hydrochloric Acid Potassium Hydroxide 2,4-Dinitrophenylhydrazine	Absorbance (reddish-brown) read at 480 nm.
	n-Butyraldehyde	1	40				
	iso-Butyraldehyde	1	40				
Aldehydes	Formaldehyde	3	600	5a	Colourimetric	Chromotropic Acid Disodium Salt Sulphuric Acid	Absorbance (purple) read at 570 nm. In soil, brown colour results so 570 nm may not be suitable.
Aldehydes	n-Butyraldehyde	10	-	2d	Titrimetric	Methyl Cellosolve Hydroxylamine Hydrochloride Potassium Hydroxide Formic Acid Phenolphthalein indicator, 1% in alcohol. Methanol Nitric Acid Thymol Blue Dimethylformamide	Colour changes from yellow to orange. Endpoint is difficult to detect. Not suitable for analysis in soil. Large amounts of water may interfere.
	iso-Butyraldehyde	10	-				

TABLE 1 (con't)

SUCCESSFUL METHODS

CLASS	COMPOUNDS DETECTED FROM EETD PRIORITY LIST	LOWER DETECTION LIMIT		REF. SOURCE	TYPE OF TEST	REAGENTS NEEDED	COMMENTS
		Water (mg/L)	Soil (mg/kg)				
Aldehydes	Formaldehyde n-Butyraldehyde iso-Butyraldehyde	10 40 20	* * *	2e	Titrimetric	Potassium Hydroxide Potassium Chloride Potassium Iodide Mercuric Chloride Mercuric Iodide Agar Iodine Sodium Thiosulfate Starch Acetic Acid	Determines aldehydes in the presence of ketones.
Aldehydes	Formaldehyde n-Butyraldehyde iso-Butyraldehyde	50 60 60	* * *	5b	Titrimetric	Bromophenol Blue Indicator Sodium Hydroxide, 50% Hydroxylamine Hydrochloride Hydrochloric Acid Ethanol	Colour changes from purple to yellow-green.
Acid Anhydrides	Acetic Anhydride	15	*	7	Colourimetric	Ethanol Hydrochloric Acid Ferric Chloride Hydroxylamine Hydrochloride Sodium Hydroxide	Absorbance (magenta) read at 525 nm. Samples need to be heated in a water bath.
Acid Anhydrides	Maleic Anhydride Phthalic Anhydride	60 150	1000 >10,000	6	Colourimetric	Phenylhydrazine Hydrochloride Potassium Ferricyanide Sodium Hydroxide Isopropanol	Absorbance (orange) read at 535 nm.
Ketones	Acetone Methyl Ethyl Ketone Methyl Isobutyl Ketone	10 10 15	150 150 400	2c	Colourimetric	Methanol Pyridine Hydrochloric Acid Potassium Hydroxide 2,4-Dinitrophenylhydrazine	Absorbance (reddish-brown) read at 480 nm.
Ketones	Acetone Methyl Ethyl Ketone Methyl Isobutyl Ketone	10 10 25	200 200 500	2d	Titrimetric	Methyl Cellosolve Hydroxylamine Hydrochloride Potassium Hydroxide Formic Acid Phenolphthalein indicator, 1% in alcohol Methanol Nitric Acid Thymol Blue Dimethylformamide	Colour changes from yellow to orange. Endpoint is difficult to detect. Large amounts of water may interfere.
Ketones	Acetone Methyl Ethyl Ketone Methyl Isobutyl Ketone	30 60 30	* * *	5b	Titrimetric	Bromophenol Blue Indicator Sodium Hydroxide, 50% Hydroxylamine Hydrochloride Hydrochloric Acid Ethanol	Colour changes from purple to yellow-green.
Ketones	Acetone Methyl Ethyl Ketone Methyl Isobutyl Ketone	40 60 50	* * *	8a	Colourimetric	Salicylaldehyde Ethanol Sodium Hydroxide	Absorbance (red) read at 460 nm.
Ketones	Acetone Methyl Ethyl Ketone Methyl Isobutyl Ketone	400 200 1600	* * *	8b	Colourimetric	o-Nitrobenzaldehyde Sodium Hydroxide Chloroform	Absorbance read at 420 nm for MEK and at 595 nm for MIK and Acetone.

TABLE 1 (con't)

SUCCESSFUL METHODS

CLASS	COMPOUNDS DETECTED FROM EETD PRIORITY LIST	LOWER DETECTION LIMIT Water (mg/L)	Soil (mg/kg)	REF. SOURCE	TYPE OF TEST	REAGENTS NEEDED	COMMENTS
Acetates	Vinyl Acetate	20	*	7	Colourimetric	Ethanol Hydrochloric Acid Ferric Chloride Hydroxylamine Hydrochloride Sodium Hydroxide	Absorbance (magenta) read at 525 nm. Samples need to be heated in a water bath.
Acetates	Vinyl Acetate	30	*	2f	Titrimetric	Bromine Sodium Bromide Methanol Potassium Iodide Sodium Thiosulfate	Yellow colour disappears.
Acetates	Vinyl Acetate	40	*	2a	Titrimetric	Mercuric Acetate Methanol Potassium Hydroxide Sodium Bromide Phenolphthalein, indicator, 1% in alcohol Chloroform	Colour changes to pink.
Amines	Morpholine	10	*	9a	Colourimetric	37% Formaldehyde Sodium Borate Carbon Disulfide Copper Sulfate Triton X-100	Absorbance (brown) read at 430 nm.
Amines and Nitriles	Morpholine Acrylonitrile	100 50	* *	2g	Titrimetric	Acrylonitrile or Morpholine Methanol Methyl Cellosolve Dimethylformamide Acetic Anhydride Perchloric Acid Thymol Blue Xylene Cyanol	
Amines	Ethanolamine	0.2	*	2h	Colourimetric	Triethanolamine Salicylaldehyde Cupric Chloride Carbon Disulfide Methanol Diethanolamine n-Hexanol	Absorbance read at 430 nm.
Amines	Ethanolamine	5	*	2b	Titrimetric	Sodium Bicarbonate Starch Chloroform Iodine Potassium Iodide Sodium Hydroxide Arsenous Oxide Sulphuric Acid Periodic Acid	Colour changes to purple-red.
Amides	Urea	0.1	*	9b	Colourimetric	Sulphuric Acid Phosphoric Acid Diacetyl Monoxime Thiosemicarbazide Phenylmercuric Acetate Potassium Chloride	Absorbance (pink) read at 525 nm.
Amides	Urea	2	*	10	Colourimetric	Ethanol Hydrochloric Acid p-Dimethylaminobenzaldehyde	Absorbance read at 425 nm.
Hydroperoxides	Hydrogen Peroxide	0.2	*	2i	Colourimetric	Sodium Iodide Acetic Anhydride	Absorbance (yellow) read at 430 nm.
Hydroperoxides	Hydrogen Peroxide	5	*	14a	Colourimetric	o-Tolidine Sodium Acetate Buffer pH 4.63 Ferrous Sulphate Ethanol	Absorbance (yellow) read at 450 nm.

TABLE I (con't)

SUCCESSFUL METHODS

CLASS	COMPOUNDS DETECTED FROM EETD PRIORITY LIST	LOWER DETECTION LIMIT		REF. SOURCE	TYPE OF TEST	REAGENTS NEEDED	COMMENTS
		Water (mg/L)	Soil (mg/kg)				
Organic Halides	Carbon Tetrachloride	50	*	11	Colourimetric	Ether Pyridine Sodium Hydroxide	Absorbance (pink) read at 500 nm for CCl_4 and $CHCl_3$ and (mauve) read at 450 nm for $C_2H_4Br_2$.
	Chloroform	5	*				
	Ethylene Dibromide	200	*				

* These methods have not been tried as yet in soil analysis.

TABLE 2

UNSUCCESSFUL METHODS

CLASS OF COMPOUNDS	REF. SOURCE	TYPE OF TEST	REAGENTS USED	COMMENTS
Aromatics	9c	Colourimetric	Aluminum Chloride Chloroform	No colour change.
Aromatics	8c	Colourimetric	37% Formaldehyde Sulphuric Acid Hexane Ether Chloroform Acetic Acid	Precipitate forms and cannot be easily dissolved.
Alcohols	8d	Colourimetric	Carbon Disulfide Sodium Hydroxide Ammonium Molybdate Sulphuric Acid Chloroform Ether	Not quantitative at levels practical for field use.
Alcohols	8e	Colourimetric	Vanadium 8-Hydroxyquinoline Acetic Acid Benzene Nitric Acid	Difficulty in preparing the reagent.
Alcohols	2j	Colourimetric	3,5-Dinitrobenzoyl Chloride Pyridine Hydrochloric Acid n-Hexane Acetone Sodium Hydroxide	No colour change.
Glycols	8f	Colourimetric	Sodium Sulfanilate Sodium Nitrite Naphthylamine Ethanol Boric Acid	Not quantitative.
Aldehydes	8g	Colourimetric	Hydrogen Peroxide Acetic Acid Phenylenediamine Ethanol	Not quanitative.
Butyraldehydes	8h	Colourimetric	Dianilinoethane Acetic Acid	Quantitative in a short range but it is above levels practical for field use.
Acid Anhydrides	8i	Colourimetric	Lanthanum Nitrate Iodine Ammonium Hydroxide	Not quantitative.
Acid Anhydrides	2k	Titrimetric	Morpholine Hydrochloric Acid Methyl Yellow Methylene Blue Methanol	Not quantitative at levels practical for field use.
Ketones	8j	Colourimetric	o-Dinitrobenzene Potassium Hydroxide Ethanol Ether	Not quantitative at levels practical for field use.
Ketones	8k	Colourimetric	Sodium Nitroprusside Sodium Hydroxide Acetic Acid	Results are quantitative but not reproducible.
Ketones	8l	Colourimetric	Sodium Bisulfite Starch Iodine	Colour change is not dependent on Ketones.
Acetates	8m	Colourimetric	Ferric Chloride Hydrate Methanol	Not quantitative.

TABLE 2 (con't)

UNSUCCESSFUL METHODS

CLASS OF COMPOUNDS	REF. SOURCE	TYPE OF TEST	REAGENTS USED	COMMENTS
Morpholine	8n	Colourimetric	Thiodiphenylamine Bromine Methanol	Not quantitative.
Morpholine	8o	Colourimetric	Copper Sulphate Carbon Disulfide Benzene	Not quantitative.
Amines	8p	Colourimetric	Chloro-2,4-dinitrobenzene Ether	Colour development takes too long for field use.
Amines	21	Titrimetric	Carbon Disulfide Isopropanol Pyridine Sodium Hydroxide Phenolphthalein	There is not much difference in the amount of titrant added between samples of varying concentrations. The endpoint is unstable and therefore hard to detect.
Amides and Nitriles	12	Colourimetric	Ferric Chloride Ethanol Hydroxylammonium Chloride Propylene Glycol Potassium Hydroxide	This method is not practical for field use because the samples need to be heated to the boiling temperature of propylene glycol, a precipitate may form depending on the amount of ferric chloride added, and the results are not consistent.
Epoxides	2m	Titrimetric	Chlorobenzene Crystal Violet Indicator Acetic Acid Hydrogen Bromide	Water interferes.
Hydrogen Peroxide	14	Colourimetric	Ferric Chloride Potassium Ferricyanide	Colour fades very quickly and results are not fully reproducible.
Alcohols, Peroxides, and Amines	2n	Titrimetric	Perchloric Acid Ethyl Acetate Acetic Anhydride Pyridine Phenolphthalein, 1% in alcohol Potassium Hydroxide Methanol	Results are very erratic. Water may interfere.
Carbon Disulfide	8q	Colourimetric	Copper Sulfate Ammonium Hydroxide Piperidine	Not quantitative.
Carbon Disulfide	5c	Titrimetric	Potassium Bromate Potassium Bromide Acetic Acid Hydrochloric Acid Starch	Not quantitative. Water may interfere.
Titanium Dioxide	14h	Colourimetric	Salicyclic Acid Tetraphenylarsonium Chloride Sodium Acetate Buffer pH 4.63 Chloroform	No colour change. May only be suitable for other titanium compounds.

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TABLE 3
ANALYTICAL CAPABILITY FOR THE LEVEL 2 SYSTEM

AIR

Immediate Capability

Acetic Acid
Acetic Anhydride
Acetone
Acetylene
Acrylonitrile
Ammonia
Benzene
Butadiene
Butanol
Butylene
Butyraldehydes
Carbon Disulfide
Carbon Tetrachloride
Chloroform
Fresh Crude Oil
Cyclohexane
Dichlorobenzene
Dichloroethane
Dimethyl Ether
Ethanol
Ethylbenzene
Ethylene
Ethylene Dibromide
Ethylene Oxide
Ethyl Hexanol
Fluorochloromethanes
Formaldehyde
Gasoline
Heptane
n-Hexane
Hydrogen Sulfide
Isopropanol
Methane
Methanol
Methylamines
Methylene Chloride
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Methacrylate
Morpholine
Propylene
Propylene Glycol
Propylene Oxide
Styrene
Toluene
Turpentine
Vinyl Acetate
Vinyl Chloride
Xylenes

Planned Capability for 1986

None

TABLE 3 (continued)
ANALYTICAL CAPABILITY FOR THE LEVEL 2 SYSTEM

WATER

Immediate Capability

Acetic Acid
Adipic Acid
Aluminum Chloride
Aluminum Hydroxide
Aluminum Sulfate
Ammonia
Ammonium Chloride
Ammonium Nitrate
Ammonium Phosphates
Ammonium Sulfate
Barium Sulfate
Benzoic Acid
Boric Acid
Calcium Carbonate
Calcium Chloride
Calcium Hydroxide
Calcium Hypochlorite
Calcium Oxide
Calcium Phosphate
Chlorine
Copper Sulfate
Ferric Chloride
Formic Acid
Hydrogen Chloride/Acid
Hydrogen Fluoride/Acid
Lead Chromate
Lead Oxides
Magnesium Hydroxide
Nitric Acid
Nitrilotriacetic Acid
Phenols
Phosphoric Acid
Potash
Potassium Hydroxide
Potassium Sulfate
Sodium Arsenite
Sodium Chlorate
Sodium Chloride
Sodium Cyanide
Sodium Hydroxide
Sodium Phosphate
Sodium Silicates
Sodium Sulfate
Sulfuric Acid (and Oleum)
Sulfuryl Chloride
Zinc Chloride
Zinc Oxide
Zinc Sulfate

Planned Capability for 1986

Acetic Anhydride
Acetone
Acrylonitrile
Benzene
Butyraldehydes
Carbon Tetrachloride
Chloroform
Cresol
Cumene
Ethanolamine
Ethylbenzene
Ethylene Dibromide
Ethylene Glycol
Formaldehyde
Hydrogen Peroxide
Maleic Anhydride
Methanol
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Morpholine
Nonylphenol
PCBs
Phenols
Phthalic Anhydride
Propylene Glycol
Styrene
p-Terphenyl
Toluene
Urea
Vinyl Acetate
Xylenes

TABLE 3 (continued)
ANALYTICAL CAPABILITY FOR THE LEVEL 2 SYSTEM

SOIL

Immediate Capability

None

Planned Capability for 1986

- Acetic Acid
- Acetone
- Adipic Acid
- Aluminum Chloride
- Aluminum Hydroxide
- Aluminum Sulfate
- Ammonia
- Ammonium Chloride
- Ammonium Nitrate
- Ammonium Phosphates
- Ammonium Sulfate
- Barium Sulfate
- Benzene
- Benzoic Acid
- Boric Acid
- Butyraldehydes
- Calcium Carbonate
- Calcium Chloride
- Calcium Hydroxide
- Calcium Hypochlorite
- Calcium Oxide
- Calcium Phosphate
- Chlorine
- Copper Sulfate
- Cresol
- Cumene
- Ethanolamine
- Ethylbenzene
- Ethylene Glycol
- Ferric Chloride
- Formaldehyde
- Formic Acid
- Hydrogen Chloride/Acid
- Hydrogen Fluoride/Acid
- Lead Chromate
- Lead Oxides
- Magnesium Hydroxide
- Maleic Anhydride
- Methanol
- Methyl Ethyl Ketone
- Methyl Isobutyl Ketone
- Nitric Acid
- Nitrilotriacetic Acid
- Nonylphenol
- PCBs
- Phenols
- Phosphoric Acid
- Potash
- Potassium Hydroxide
- Potassium Sulfate
- Propylene Glycol
- Sodium Arsenite
- Sodium Chlorate
- Sodium Chloride
- Sodium Cyanide
- Sodium Hydroxide
- Sodium Phosphate
- Sodium Silicates
- Sodium Sulfate
- Styrene
- Sulfuric Acid (and Oleum)
- Sulfuryl Chloride
- p-Terphenyl
- Toluene
- Urea
- Vinyl Acetate
- Xylenes
- Zinc Chloride
- Zinc Oxide
- Zinc Sulfate

EVAPORATION FROM PCB MIXTURES

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EVAPORATION FROM PCB MIXTURES

Abstract

Using reported equilibrium vapour pressures over a PCB mixture (Aroclor 1254), both laboratory experiments and field data indicate that evaporation models overestimate the mass transfer from PCB mixtures. Laboratory experiments determining evaporation rates for PCB mixtures between 26°C and 100°C produced results which were between 1/66 and 1/50 of model results calculated using minimum estimates of the gas phase mass transfer rates. Similarly, field data gave PCB air concentrations which were two orders of magnitude lower than model results from a combined spill evaporation equation and a ground level source despersion model. The reasons for such discrepancies are not certain but some possibilities are:

1) non-ideal behaviour of PCB mixture vapour pressures,
2) liquid phase resistance, and
3) errors in reported equilibrium mixture vapour pressures.

1. INTRODUCTION

The possible effects of Poly-Chlorinated Biphenyls (PCB) on human health makes evaporation from a PCB spill an important environmental problem. Evaporation from a liquid can be computed by assuming that there exists a thin layer above the surface where concentrations of evaporated gas are in equilibrium with liquid surface concentrations of the substance. At steady state, the mass transfer at the upper boundary of this gas layer balances the flux from the liquid surface into this layer.

For a pure liquid the evaporation rate then depends upon the liquid's temperature which determines the equilibrium vapour pressure in the thin layer above the surface and on the gas phase mass transfer rate which can be due to either free or forced convection with molecular diffusion in still air providing a lower bound on the mass transfer rate. Liquid mixtures on the other hand can provide a more complex system when evaluating evaporation rates since steady state evaporation depends on both the gas phase mass transfer rate and on the flux of material from the liquid surface into the thin layer of air above it. In this paper we will compare evaporation rates for PCB mixtures and gas phase mass transfer coefficients. We will also present a comparison of measured PCB concentrations near a Waste Management site with results from a combined spill evaporation - ground level dispersion model.

A wide range of PCB molecules exist and these molecules can be organized into groups depending on their number of chlorine atoms. Each of these groups contains a number of isomers. Most existing supplies of PCB's are commercial mixtures of these various molecules. While most individual chlorobiphenyls are solids at room temperature, these commercial mixtures range from mobile oils to sticky resins.

From the point of view of evaporation, the most striking property of PCB compounds is the orders of magnitude variations found in vapour pressures for the compound groups (Bidlemann, 1984). Table 1 presents molecular weights and average vapour pressures at 25°C derived by Bidlemann (1984) for a range of PCB compound groups. Also presented on this table are average mole fractions of the PCB compounds groups making up the commercial mixture Aroclor 1254 produced by the Monsanto Corporation (presented in "The Chemistry of PCB's", 1974).

2. LABORATORY INVESTIGATIONS OF EVAPORATION OF AROCLOR 1254

Several laboratory investigations of evaporation from PCB mixtures have been reported in the literature. Haque et al. (1974) gravimetrically measured evaporation from planchets having a 5.07 cm^2 exposed area of Aroclor 1254 at 26°C and heated to 60°C. Over a 30 day period they found evaporation rates of 2.3×10^{-7} $gm^{-2}s^{-1}$ and 9.9×10^{-6} $gm^{-2}s^{-1}$ for 26°C and 60°C respectively. Within experimental error these evaporation rates were constant over the 30 day period. Although error bars were not reported for these evaporation rates, Figure 4 in Haque et al. (1974) indicates an error of at most ± 50% for the 26°C evaporation rate and ± 10% for the 60°C evaporation rate. A report by Monsanto Corporation (Tech. Bull OPL-306) gave evaporation rates from a container with surface area of 12.28 cm^2 for a number of Aroclor mixtures at 100°C. For Aroclor 1254 this report gave an evaporation rate of 1.47×10^{-4} g $m^{-2}s^{-1}$ in a 24 hour test.

In this section we will compare these observed evaporation rates with those determined from equilibrium vapour pressures for the Aroclor 1254 mixture and gas phase mass transfer coefficients. For the two heated cases (60°C and 100°C) gas phase mass transfer is modelled by analogy with the convective heat transfer coefficient. Since these evaporation experiments were performed in vented fume hoods there would also be a component of forced convection to augment the gas phase transfter. This component of the gas phase transfer could not be evaluated since the flow conditions during these experiments were not known.

The heat transfer coefficient h(cal $s^{-1}{}^{o}C^{-1}m^{-2}$) for a horizontal surface of lateral dimension L_1(m) is given as follows (Chapman, 1967):

$$h = 0.32\ (\Delta T/L_1)^{\frac{1}{4}} \qquad (1)$$

for laminar flow and

$$h = 0.36\ (\Delta T)^{1/3} \qquad (2)$$

for turbulent flow. Here $\Delta T = Ts - Ta$ where Ts is the liquid surface temperature and Ta is the ambient air temperature. ΔT is in °C. Since we expect laminar flow to exist in these experiments equation (1) is used.

The heat transfer coefficient is related to diffusivity α(m^2S^{-1}) by

$$h\Delta T = \alpha(\Delta T/\Delta Z)\rho Cp \qquad (3)$$

where ρ is the density and Cp is the specific heat of air at temperature (Ts + Ta)/2 and ΔZ is a diffusion layer length scale in the vertical. Defining $\alpha/\Delta Z$ as a velocity W_h(ms^{-1}), we note that

$$W_h = h/\rho C_p \qquad (4)$$

where W_h may be interpreted as a velocity scale of heat transfer due to convective currents which exist above a heated surface.

Assuming the heat transport across the laminar heat diffusion layer depends only on the conductivity of air while mass transport across a similar mass diffusion layer depends only on molecular diffusion then heat and mass transfer coefficients can be related by (Chapman, 1967)

$$W_m = W_h(Pr/Sc)^{0.67} \qquad (5)$$

where Pr is the Prandtl number for air and Sc is the Schmidt number for PCBs.

If W_h were entirely due to bulk transport corresponding to convective currents extending down to the liquid surface then W_m would be equal to W_h. The convective mass transfer coefficient probably lies between these extremes. For mass transfer of PCBs, equation (5) gives a minimum mass transfer value since Pr = 0.7 while Sc = 3.0. In the following calculations equation (5) will be used as providing the maximum gas phase resistance to evaporation. Forced convection would increase the gas phase mass transfer and could be the dominant mechanism for mass transfer if a moderate ventilation rate were used in the fume hoods (see Chapman (1965, p. 329).

For the Haque et. al. (1974) experiment at Ts = 60°C, Ta = 20°C, L = 0.022m, Pr = 0.7 and Sc = 3.0, equations (1), (4) and (5) give

$$W_m = 0.29 \text{ cm s}^{-1}.$$

Using the Monsanto experimental data with Ts = 100°C, Ta = 20°C, L = 0.035, Pr = 0.7 and Sc = 3.0, the mass transfer coefficient becomes

$$W_m = 0.33 \text{ cms}^{-1}.$$

The equilibrium concentration, Co (gm^{-3}), of PCB within the thin layer just above the surface is given by

$$Co = \frac{P\ M}{R\ T} \qquad (6)$$

where P is vapour pressure (Pa), M is the molecular weight ($g\ mole^{-1}$) and R is the ideal gas constant ($8.34\ J\ mole^{-1}\ {}^{o}K^{-1}$).

Equilibrium vapour pressures for the Aroclor 1254 mixture are derived from measurements presented in the Hygienic Guild Series (1965). Interpolating 60°C and 100°C data points from a logarithmic plot of this data yields 1.8 Pa at 60°C and 19 Pa at 100°C. For comparison, extrapolation of vapour pressure data for Aroclor 1254 presented by Monsanto Corporation (Tech. Bull. OPL-306) for temperatures above 150°C gives 0.7 Pa at 60°C and 10.8 Pa at 100°C. Since these two sources agree on vapour pressures above 150°C where both have observations, interpolations from the Hygienic Guild Series data are used. Using an average molecular weight of 327 for Aroclor 1254, equation (6) then gives 0.225 $g\ m^{-3}$ at 60°C and 2.24 $g\ m^{-3}$ at 100°C for C_o. The evaporation rate (E) is given by

$$E = W_m\ Co \qquad (7)$$

which yields $6.5 \times 10^{-4} gm^{-2}s^{-1}$ at 60°C and $7.4 \times 10^{-3}\ gm^{-2}s^{-1}$ at 100°C

The evaporation rates derived using the gas phase mass transfer coefficient in equation (7) are 66 and 50 times the observed values at 60°C and 100°C respectively. Since the minimum gas phase mass trransfer coefficients were used in equation (7), these results indicate that the steady state concentrations of PCB in the thin layer just above the surface are at least a factor of 50 to 66 less than indicated by the equilibrium vapour pressures used in these calculations.

Calculating a gas phase mass transfer coefficient for evaporation at 26°C is difficult without knowing the flow conditions in the fume hoods. A minimum mass transfer rate of 1×10^{-3} ms^{-1} corresponding to molecular diffusion of mass in still air was used by MacKay and Yeun (1983). Using this minimum value for Wm and an equilibrium vapour pressure of 0.09 Pa for Aroclor 1254 at 26°C equations (6) and (7) yield an evaporation rate of 1.2×10^{-5} $gm^{-2}s^{-1}$. This is 52 times the observed evaporation rate of 2.3×10^{-7} $gm^{-2}s^{-1}$. Since forced convection would give much higher values for Wm with quite moderate flow rates (i.e.$\sim\frac{1}{2}$ m s^{-1}), the discrepancy between observed and calculated evaporation rates is likely larger than indicated by the above calculations (Chapman, 1967).

3. FIELD MEASUREMENTS OF EVAPORATION OF PCB MIXTURES

Evaporation from an open liquid surface is modelled in two parts. The first part is a model of the rate of evaporation for the pool while the second is a dispersion model of a ground level source occupying a finite area. Downwind concentrations are derived from the combination of the two models.

Mackay and Matsugu (1973) gave the following formula for the gas phase mass transfer needed to give an evaporation rate:

$$W_m = 0.0048U^{0.78}d^{-0.11}Sc^{-.067} \qquad (8)$$

Here Wm is the gas phase mass transfer coefficient (m s^{-1}), U is the wind speed (ms^{-1}), d is the pool length (m) and Sc is the Schmidt number (dimensionless) for the evaporating gas concerned,

$$Sc = V/D. \qquad (9)$$

Here V is the viscosity of air and D is the diffusivity of the evaporating gas.

Substituting W_m from equation (8) and Co from equation (6) in equation (7) gives the evaporation rate.

The second aspect of the model is the dispersion of the PCB material evaporated from the spill. A set of standard equations evaluated for either neutral (Pasquill-Gifford class D stability) or stable (Pasquill - Gifford class E or F stability) atmospheric conditions are used. This model was adapted from the ground level release model of Van Ulden (1978).

The basic equation for ground level concentrations due to a ground level source is

$$\frac{C}{Q} = \frac{0.73}{\sqrt{2\pi}\ \bar{Z}\bar{U}\sigma_y} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \qquad (10)$$

where C is the concentration in gm^{-3}, $\bar{Z}$ is the depth in m over which the contaminants are well mixed at a downwind distance X, $\bar{U}$ is the mean wind speed (ms^{-1}) over the depth Z, y is the crosswind distance from the plume's centreline (m), σ_y is the crosswind dispersion parameter (m) and Q is the source strength (gs^{-1}) given by

$$Q = E\,A$$

where A is the area of the spill (m^2).

The dispersion parameter σ_y is given by

$$\begin{aligned}
\sigma_y &= \left[(0.1X)^2+(H/4)^2\right]^{\frac{1}{2}} && \text{NEUTRAL} \\
&= \left[(0.06X)^2+(H/4)^2\right]^{\frac{1}{2}} && \text{STABLE (E)} \\
&= \left[(0.04X)^2+(H/4)^2\right]^{\frac{1}{2}} && \text{STABLE (F)} \qquad (11)
\end{aligned}$$

where H (m) is the length scale of the spill and X (m) is downwind distance. The above formulation for σ_y then takes into account the finite size of the source.

The depth $\bar{Z}$ over which the contaminants are mixed is

$$\begin{aligned}
\bar{Z} &= 0.21 \; Z_o(X/Zo)^{0.8} && \text{NEUTRAL} \\
&= 1.0 \; Z_o(X/Zo)^{0.5} && \text{STABLE (E)} \\
&= 0.5 \; Z_o(X/Zo)^{0.5} && \text{STABLE (F)} \qquad (12)
\end{aligned}$$

where Z_o is the surface roughness length which is taken as 0.01 m for the flat terrain to be modelled.

A friction velocity U_* (m s^{-1}) is defined as

$$U_* = \frac{K\,U(z)}{\ln(Z/Zo)} \qquad \text{NEUTRAL AND STABLE (E)} \qquad (13)$$

$$= \frac{K\,U(Z)}{\ln(Z/Zo)+4.7\,Z/L} \qquad \text{STABLE (F)}$$

$$L \approx 1100\,U_*^2 \qquad (14)$$

where K = 0.4 is the Karman constant, U(Z) is the observed wind speed at height Z in m and L is the Monin-Obukhov length in m. L depends on U_* and surface heat flux.

Using the friction velocity U_* and the layer depth Z, an average layer velocity U (m s^{-1}) is given by

$$U = \frac{U_*}{K} \ln (0.6\ \bar{Z}/Zo) \qquad \text{NEUTRAL AND STABLE (E)}$$

$$= \frac{U_*}{K}\left[\ln (0.6\ \bar{Z}/Zo) + 4.7\ \bar{Z}/L\right] \qquad \text{STABLE (F)} \quad (15)$$

This completes the set of equations defining ground level concentrations due to evaporation from a liquid pool.

An ambient air survey in the vicinity of the PCB Chemical - Waste Management disposal site in Smithville, Ontario was conducted by the Ontario Ministry of the Environment between September 23 and November 26, 1980. In this survey 24 h average ground level concentration of PCBs were recorded at 4 sites adjacent to the compound fence and 10 other sites located in different directions at a variety of distances from the storage site. Daily monitoring took place at all 14 sites from September 23 to October 15, 1980 with weekly monitoring at 10 sites from October 21 to November 26, 1980. Figure 1 shows the monitoring sites located within 300 m of the disposal site. The site is located in a generally flat, open area with a small stand of trees located about 150 m east of the fenced-in complex.

Air samples were 24 hour average values usually taken from 11 a.m. to 11 a.m. the following day. During this 24 hour period, the samplers (located 1 m above the ground) pumped ambient air through cartridges which were subsequently analysed for PCB content.

Overall the data at the 4 fenceline sites showed lower concentrations on days when the temperatures were lower. This was expected since PCB mixture vapour pressures are a strong function of temperature and the evaporation rate will therefore decline with temperature. After taking into account these temperature effects the data indicates a reasonably constant source size during the observation period. Ontario Environment Ministry personel estimated the average area of the PCB evaporation source to be 240m^2. Although this source was made up of several pools or wet surfaces it is modelled as one pool located at the centre of the compound.

Sites 5, 6, 9, 13 and 14 were used in the intercomparison of model and observed PCB concentrations. The days selected for analysis were those where a reasonably constant wind direction blowing over a monitoring site was maintained for a significant portion of the 24 h period. In the model, 24 h average concentrations are derived using hourly wind speed and direction data as input to the ground level source dispersion model with the output summed and averaged over 24 hours. Wind direction (and speed) data was available at intervals of $22\frac{1}{2}^{\circ}$ (i.e. N, NNE, NE, etc.) from Hamilton Airport (~15 km north of Smithville). The average contribution of a plume at a monitoring site was calculated by averaging 23 positions of the plume centreline over $\pm 11^{\circ}$ from the stated wind direction. This takes into account the lack of precise information about the crosswind distance between the plume and the monitoring site.

To determine vapour pressures for use in equation (3) hourly temperatures from Hamilton Airport were used. Vapour pressures were interpolated from a logarithmic plot of equilibrium vapour pressure versus temperature derived from data published in the Hygienic Guild Series (1965). The Smithville disposal site handles a variety of PCB mixtures (Aroclor 1016 and 1254) with different equilibrium vapour pressures. Vapour pressures corresponding to the less volatile Aroclor 1254 mixture are used in these calculations since they produce the likely lower limit on model concentrations.

The above analysis was performed for 11 observations from the Smithville data set. The results are presented in Table 2. An average ratio of predicted to measured concentrations of 310 was found. Overall the calculated concentrations were very well correlated with observed values despite their large difference in magnitude. The correlation coefficient of r = 0.87 indicates that the dispersion model does a good job at predicting the fall off of concentration with distance from the source and with the frequency of occurrence of winds passing over a given monitoring site.

The relative proportions of PCB mixtures (Aroclor 1254, 1016 etc.) at the storage site and the area of exposed surface are both variable quantities which were not well defined during the observation period. Therefore the ratio between calculated and observed PCB concentrations is not really well defined since the exact source strength is not known. The results in Table 2 nevertheless show that the model produces concentrations which are two orders of magnitude larger than observed PCB concentrations.

4. FACTORS AFFECTING EVAPORATION RATES

Although the reasons for the large discrepancies between calculated and observed evaporation rates are not known, several possibilities are suggested here.

a) Comparing the Aroclor 1254 mixture equilibrium vapour pressure of 0.08 Pa at 25°C derived from the Hygienic Guild Series (1965) data with vapour pressures of individual component groups making up Aroclor 1254 (Table 1) shows that the mixture equilibrium vapour pressure is biased towards the lower chlorine content, more volatile PCB's. This indicates that either

   1) the mixture equilibrium vapour pressures are too high, or
   2) the PCB mixture behaves in a non-ideal manner.

   A non-ideal behaviour of mixture vapour pressures could be related to the range of vapour pressures shown in Table 1 coupled with the fact that many of the PCB component groups are solids at room temperature while the mixture is a viscous liquid.

If one assumes that the Hygienic Guild equilibrium vapour pressures are incorrect, a vapour pressure corresponding to the bulk mixture composition and vapour pressures in Table 1 (for 25°C) can be derived. This mixture vapour pressure is quite dependent on the small fraction of $C_{12}H_{10}$ and $C_{12}H_9Cl$. Using 0.05% for these two compound groups produced a mixture vapour pressure of 0.009 Pa. This is 11% of the value derived from the Hygienic Guild series at 25°C. If all of the Hygienic Guild Series vapour pressures are scaled by this factor of 0.11, the calculated and observed laboratory evaporation rates are:

Temperature(°C)	Evaporation ($gm^{-2}s^{-1}$)		Cp/Cob
	Cp: Calculated	Cob: Observed	
26	1.3×10^{-6}	2.3×10^{-7}	5.7
60	7.2×10^{-5}	9.9×10^{-6}	7.3
100	8.1×10^{-4}	1.47×10^{-4}	5.5

Therefore even when vapour pressures corresponding to an ideal mixture with bulk composition as given in Table 1 are used, the calculated evaporation rates are still 6 or 7 times the laboratory observed evaporation rates.

b) Aroclor 1254 is described as a viscous liquid. A number of authors (Mackay and Matsugu (1973), Mackay and Yeun (1983) Broecker and Peng (1974), Wolfe and Heijde (1982)) have discussed the effects of liquid phase resistance in multicomponent liquids. When both liquid and gas phase resistances are present, evaporation from a liquid surface is determined by

$$\frac{1}{W_{mt}} = \frac{1}{W_{ml}} + \frac{RT}{HW_{mg}} \qquad (16)$$

Here W_{mg}, W_{ml} and W_{mt} are the gas, liquid and overall mass transfer coefficients while H is the Henry's law constant for the mixture concerned. A third term could be added to equation 8 if a surface resistance were present.

Which combination of the above factors might account for the large calculated evaporation rates is not clear.

5. SUMMARY

Calculations using minimum values for gas phase mass transfer along with equilibrium vapour pressures over a PCB mixture give evaporation rates much larger than those observed. These results indicate that more laboratory studies of evaporation from viscous complex mixtures are needed. A study in which gas phase transfer rates were determined from evaporation rates for a pure substance with a molecular weight similar to that in the complex mixture would be very informative. Using an experimentally determined gas phase mass transfer rate along with mixture equilibrium vapour pressures in equations (6) and (7) would clearly define the extent to which gas phase transfer can account for observed evaporation from complex mixtures. Since evaporation rates from environmental spills are determined using gas phase mass transfer coefficients and vapour pressure data the results of this type of experiment would be very significant.

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TABLE 1

PCB Group	Molecular Weight	Average[a)] Vapour Pressure (25°C)(Pa)	% Composition[b)] of Aroclor 1254
$C_{12}H_{10}$	154	6.7	$<$ 0.1
$C_{12}H_9Cl$	189	1.3	$<$ 0.1
$C_{12}H_8Cl_2$	223	0.13	0.5
$C_{12}H_7Cl_3$	258	0.07	1.0
$C_{12}H_6Cl_4$	292	0.011	21.0
$C_{12}H_5Cl_5$	326	0.0021	48.0
$C_{12}H_4Cl_6$	361	0.00053	23.0
$C_{12}H_3Cl_7$	395	0.00017	6.0

a) From Bidlemann (1984)

b) From "The Chemistry of PCB's" (1974)

TABLE 2

Site: Smithville

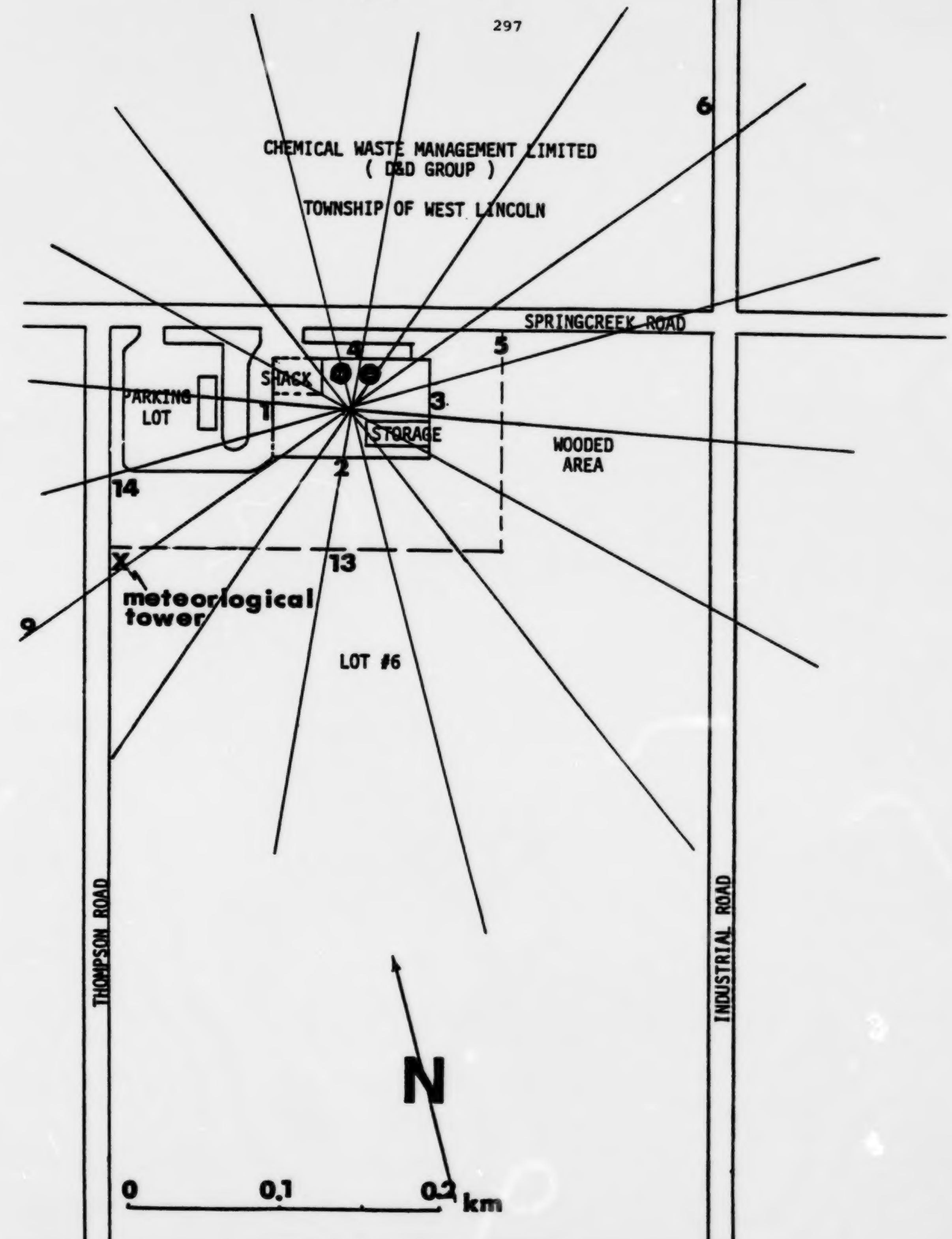
Date	Monitor No.	Distance from centre of source (m)	Calculated Cp(ng m^{-3})	Observation C_o (ng m^{-3})	Cp/Co
Oct. 4,80	5	100	14,200.	43.5	326
	6	295	1,310.	4.6	285
Oct. 5,80	5	100	14,320.	25.7	557
	6	295	987.	2.9	340
Oct. 9,80	13	100	4,460.	17.0	262
	14	150	7,950.	19.4	410
Oct.10,80	9	250	3,460.	8.6	402
	14	150	2,010.	7.3	275
	6	295	770.	3.8	203
Oct.11,80	5	100	9,700.	47.6	204
	6	295	545.	3.8	143
				Avg.	310

Note: 1) All Concentrations are 24 hr. avg. values

2) Predicted concentrations are average of 24 one hour values

3) A background concentration of 0.4 ng m^{-3} has been subtracted from observations.

Figure 1


CHEMICAL WASTE MANAGEMENT LIMITED
(D&D GROUP)
TOWNSHIP OF WEST LINCOLN
6
SPRINGCREEK ROAD
4
5
SHACK
PARKING LOT
1
3
STORAGE
WOODED AREA
2
14
X
13
meteorlogical tower
9
LOT #6
THOMPSON ROAD
INDUSTRIAL ROAD
N
0
0.1
0.2
km
LONDON ROAD

CLEANUP OF PCB'S FROM
ABANDONED DEW LINE SITES

by Lieutenant Steve Ponton
Military Engineer
Canadian Armed Forces

This paper will present a summary of a PCB cleanup operation conducted at 22 abandoned military installations located along the Distant Early Warning (DEW) radar line in the Canadian arctic. Two teams, headed by personnel from the Department of National Defence (DND) cleaned those sites during the period of 16 July - 14 August 1985. Both teams included representatives from DND, The Department of Indian Affairs and Northern Development (DIAND) and the Environmental Protection Service (EPS) in Edmonton. As well, each team was supported by one military CC-115 Buffalo airplane and two military CH-135 Huey helicopters. During this operation, approximately 7200 litres of liquid PCBs and several hundred kilograms of contaminated soil and equipment were removed. These items were packaged, inventoried and placed in 135 sealed 205-litre drums and 40 environmental containers. These drums and containers were then collected at Hall Beach, N.W.T., for transportation by the United States Air Force (USAF) to disposal sites outside Canada.

DND was first approached by DIAND in 1984 to provide assistance in cleaning up numerous abandoned military installations located in the Yukon and the Northwest Territories. That request was made for reasons such as the urgency of cleaning up those sites, the unknown extent of the work required, the isolation of the sites, and the possibly high costs of conducting such an operation by other means. Finally, the fact that DND once owned these sites surely also influenced the request.

DND accepted and tasked 1 Construction Engineering Unit (1 CEU) in Winnipeg to conduct the cleanup in the summer of 1985. The other two federal departments involved also agreed to participate directly in the project. Agreements dividing the responsibilities to plan, organize and execute the cleanup operation were prepared and signed between the three departments. DIAND accepted the responsibility to assume arctic community liaison both before and after the cleanup. DND was tasked to arrange the operation and to provide almost all the resources needed. The cleanup was prepared and conducted under the supervision of EPS which agreed to take responsibility for training DND personnel, providing on-site representatives, taking care of the site inspection, and monitoring the effectiveness of the cleanup work.

The first step in planning this project was to define the extent and limitations of the cleanup. The number of sites to be covered was narrowed down to 22, all located along the DEW Line. The remainder were scheduled for a separate cleanup operation as part of the upgrading program for the New Warning System chain of radars.

A two month period was allocated for the cleanup. Because of this time restriction, the number of sites to cover, and their isolation and relatively unknown conditions, the cleanup operation was limited to three days per site. Furthermore, the cleanup would be restricted to the removal of contaminants that could be easily located. The cleanup would be

.../2

complemented by a site inspection and in-situ soil testing for PCB concentration to determine the effectiveness of the work and to recommend future cleanup. Finally, as part of the operation, abandoned petroleum products found in the vicinity of the sites were also to be burned when practical.

With that information at hand, 1 CEU submitted to DND Headquarters in Ottawa requirements for personnel, airlift, aircraft, meals and lodging to support the project. Following that, a site recce was conducted at Ross Point, N.W.T., in March 1985. The location was chosen by EPS as being representative of an abandoned DEW Line site. A recce party of four people from the three departments travelled to and from Yellowknife on the same day using a military CC-138 Twin Otter. The recce lasted 45 minutes during which time the building and garage were inspected and PCB-filled electrical equipment was located and examined.

Based on this site visit, cleanup procedures and lists of equipment and material needed were elaborated. It soon became apparent that the lack of suitable storage facilities on the DEW Line would create a major logistical problem. The requirement was to remove the PCBs from abandoned sites and transport them ultimately to Hall Beach where the USAF would assume responsibility for them. However, proper storage regulations had to be followed even for temporary storage and even though this project was carried out in the distant and isolated arctic environment.

This problem was solved with the acquisition of 'SARASPAC' environmental containers. They are palletized (therefore portable) steel containers which meet Canadian and American requirements for a dyked covered PCB warehouse. With floor dimensions of 1.2 m X 1.5 m and a height varying from 85 to 100 cm, the SARASPAC's can store up to four 205-litre drums. They weight 150 Kg when empty and up to 1000 Kg when carrying a full load. Their weight created a problem when they were loaded or unloaded from the aircraft with the absence of a forklift at abandoned sites. They had to be moved by hand for short distances with the associated safety hazards of carrying such an awkward load over rough terrain. For longer hauls, helicopters were used.

PCBs were first stored in 205-litre drums meeting American regulations DOT-17C. Once full, these drums were inserted into the containers using either a forklift or a helicopter. The resulting combination of drums and containers enabled the cleanup teams to carry out their task with greater flexibility as they constantly had a portable 'warehouse' to store and transport PCBs as they were found, thus respecting all environmental regulations.

The remaining equipment and material necessary for the cleanup consisted of an assortment of hand and power tools, protective clothing, and a few generators and drum carts. Most of these items, as well as the aviation fuel, were obtained through the military supply system.

.../3

All of them were pre-positioned on the DEW Line at strategic locations prior to the project by an extensive airlift program of both military and civilian airplanes. 1 CEU's goal was to be self-sufficient throughout the operation in order not to rely on the incomplete and often long air resupply routes covering the arctic. Consequently, no resupply system was set up other than the already pre-positioned items. As it came out, very little outside support was required to sustain the cleanup operation besides the logistical support provided by the DEW Line stations.

The military people involved in the cleanup crew were selected from numerous bases in Canada. Along with their civilian counterparts from EPS and DIAND who took part in the operation, they converged in Winnipeg for a one day training session prior to departure to the north. The day was spent in giving introductory lectures on various subjects to the crew. The lectures covered the nature and danger of PCBs, handling measures and safety precautions, the arctic environment, and the operation details and requirements all contained in the 'Operation Order' for the cleanup. Last minute administrative details were also ironed out and a blood sampling program for PCB contamination was conducted the same day. This collection was compared to results obtained from a similar sampling program performed on all participants after the operation. A combination of commercial and military flights brought the cleanup personnel to the DEW Line the next day for the start of this project.

The cleanup operation was conducted during the period 16 July to 15 August 1985. The work was divided between two identical teams, one working on 12 sites in the western arctic and the other team on 10 sites in the eastern arctic. Each of them was made up of 28 persons, divided into a cleanup crew of 9 and an air support group of 19. Those numbers do not include the occasional presence of 'mobile' officials from EPS who moved from one team to the next with whatever means available at the time, to assist them in establishing site cleanup procedures during the first two weeks of the project.

The cleanup crew was composed of seven military personnel selected from across Canada and one EPS and one DIAND team representative. Both team leaders were from DND and included in each team was an electrician, a fire fighter, and four field combat engineers. The air support group was composed of a six-man crew with one CC-115 airplane and two CH-135 helicopters with a 13-man detachment composed of pilots, co-pilots, navigators, flight engineers and loadmasters. The CH-135 detachment also included a six-man ground maintenance crew.

Prior to the start of the operation, USAF and Canadian handling and transport regulations were obtained. EPS also prepared and issued the cleanup procedures to be followed on this project. They underwent minor changes during the operation, however those modifications were always approved by the EPS team representative prior to their implementation.

.../4

They were simple but complete and adapted to all site conditions encountered during the summer. They are summarized as follows:

a. Site Recce. A recce of the abandoned site was accomplished prior to the cleanup. Generally involved were the team leader, the EPS representative, and one helicopter. They began with an aerial sweep of the site property which aided in locating possible contaminated areas such as garbage dumps. At the end of the aerial inspection, the helicopter landed at all suspicious areas to allow the recce party to inspect the terrain. Through that process, some contaminants were found immediately and contaminated areas were defined quickly.

b. Site Sweep. The site recce was followed by a site sweep involving the whole cleanup crew spaced at 6 m intervals. Stakes and coloured ribbons were used to mark swept areas and to pinpoint locations of suspected contaminants or stains. Simultaneously, drums were also inspected for remnants of petroleum products. Building interiors were also covered and spray paint was used to highlight contaminated items inside. The sweep was first intended to cover the whole site property, but it was often restricted to a smaller area as the recce group was able to clear remote and wide areas with the helicopter.

c. Identification and Testing. The next step was to identify suspicious equipment and test stains found during the sweep. The former was easy and by the end of the operation all team members could recognize both PCB-filled items and POL products. However, problems developed with the portable PCB field testing kits. The testing procedures proved too complex to be performed in a field environment and the kit itself was too cumbersome to move daily to sites. Therefore, the on-site testing was restricted to a collection of soil samples to be analyzed afterward at the staging point or sent directly to Edmonton for analysis. In view of those problems and of the need for the EPS team representative to identify PCBs immediately, he relied instead on the proven but less technical methods. They were to smell stains and equipment to identify PCB fumes, if any, or to immerse a liquid sample in a water cup and see if the heavier PCB particles would settle at the bottom. During the identification and testing phase the EPS representative and one helper would be so employed while the rest of the team would define contamination areas, prepare tools and material, and suit up.

d. Cleanup of Contaminants.

(1) The cleanup of contaminants followed and it involved the removal of PCB-filled electrical equipment, contaminated soils, and the burning of petroleum products. Since most of the PCBs were found inside buildings, the work party began there. An efficient routine was established with

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three workers removing equipment, one packaging it and one completing the inventory. Simultaneously, two personnel were burning petroleum or otherwise helping out. When the cleanup inside the building was nearing completion, some personnel were then employed outside to remove other equipment and contaminated soil.

(2) Contaminated electrical equipment found in buildings was removed using an assortment of hand and power tools. A polyethylene sheet or an aluminum tray was first placed under each electrical cabinet to prevent any PCB dripping onto the floor. Each piece removed was then transported to a packaging area where it was wrapped in 6 mil thick polyethylene. Other equipment found loose outside or inside the building was also brought there for wrapping. Contaminated soil was removed to a depth of 0.3 metres and placed immediately in drums. Each contaminated item was inventoried and placed into new drums. These were serialized and contained 50 mm of absorbing material at the bottom. Once full, drums were sealed and inserted into SARASPAC containers using a forklift or helicopter. Equipment too large to be placed in a drum was either reduced in size by a cutting torch or placed directly in a separate container with a 50 mm layer of absorbing material at the bottom.

Contaminated tools, equipment and rubber boots that were not disposed of in drums were instead decontaminated by project personnel by wiping them down with diesel fuel. The rags used in the process were then placed in drums. The aircraft used on this operation were not judged contaminated by the EPS team representative and were not decontaminated.

Throughout the cleanup, personnel were required to wear an assortment of protective clothing including disposable suits, neoprene gloves, rubber boots, and safety helmets. Respirators were not included as they were judged as unnecessary by EPS. However, they were required at two sites where PCB was suspected of having been burned. The problem was solved by borrowing respirators at the Cape Dyer DEW station. Clothing was changed on an as required basis when damaged or contaminated. On completion of the project, every pair of used rubber safety boots was disposed of in drums.

The staging points for the cleanup teams were active DEW Line stations and CFS Inuvik. They provided meals, lodgings, communication links, aviation fuels and other services. They also served as centres to pre-position project equipment and material and as temporary storage sites for contaminants prior to their shipment to Hall Beach. The cleanup teams moved in and out of those stations on a daily basis to work at the abandoned sites. Most sites were within one hour's flying time from the staging points. Once sites around a particular staging point were cleaned, the cleanup team and supporting aircraft would relocate to the next staging point. On two occasions, only the helicopter detachment took part in this move as the new staging point could only provide limited support.

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Each team was supported by one CC-115 Buffalo and two CH-135 Huey helicopters. The Buffalo provided transportation for the project personnel, equipment and material between all the locations with a serviceable airstrip. It also established fuel caches for the helicopters and transported the drums and containers of contaminants back to the staging point and to Hall Beach whenever possible. The two airplanes logged 225 flying hours in support of this operation. A separate flight of a military CC-130 Hercules airplane moved remaining drums of contaminants from the staging points to Hall Beach after the project completion. When combining this flight with the other ones performed during the pre-positioning phase, a total of 120 hours were flown by this type of airplane.

The Hueys complemented the work of the Buffalo by moving project personnel, equipment and material back and forth from the abandoned site's runway to the operational centre of the site. They also replaced the Buffalos on the east coast of Baffin Island in carrying the above items to sites without a serviceable airstrip.[1] On those occasions, the Buffalo would move everything to the nearest active DEW station and the Hueys would ferry from there. With the exception of personnel, most equipment and all drums were slung. A steel net could carry three full drums at a time while a set of straps could only sling one. The Hueys were also used to insert drums into containers when a forklift was not available. A total of 500 flying hours were required from all the helicopters to support this operation.

The DEW System Office also supported the operation with its regular flights servicing the DEW Line and Winnipeg. Those flights were used to rotate the air support crew and to resupply some equipment to the cleanup teams during the operation; they were also used to return unused drums and containers to 1 CEU Winnipeg after the operation.

No definite working schedule was established prior to the project. Rather, team leaders had to work around the weather. Out of the 59 working days available to both teams, 12 were missed due to foggy or rainy weather, aircraft down time, or aircrew rotations. The remainder were used in the cleanup or in moving from one staging point to another.

On a typical work day, the teams would work anywhere from 8 to 15 hours, with up to two hours spent travelling. Temperatures ranged between 0°/-10°C during the day with strong winds being common. Fortunately, mosquitoes were hampered by the wind and cold and were not a nuisance on this project. Meals in the form of sandwiches were brought to the work site daily. On a moving day, the crew would move into a new staging point and pack up or unpack project items, inspect all equipment and material, and prepare for the next day. A site recce was usually done on a moving day.

A total of 135 drums of contaminants were removed during the cleanup operation; 52 by the western team and 83 by the eastern team. No exact figures have been issued by EPS on the amount of PCB that was removed, but

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[1] Ekalugad Fiord, Kivitoo, Durban Island, Padloping Island

it was estimated that 7200 litres and several thousand kilograms of contaminated soil and equipment were removed. In general, at an abandoned site where buildings were still present, the cleanup lasted two days with an average removal of 300 litres of liquid PCB contained in about 1000 kg of electrical equipment. Up to 25 kg of soil was also dug up at each site. Those contaminants were placed in six to nine drums weighing up to 200 kg each when full. Petroleum products were also burned in varying quantities at 13 sites. The amount involved was approximately 22500 litres of lubricating oil, 8000 litres of diesel fuel, and 2500 litres of engine oil. However, while all visible PCBs were removed, some petroleum was left intact at a few sites due to the impracticality and danger involved in burning them.

It is difficult to label a price tag to this cleanup operation since DND resources were used. Furthermore, the great majority of the cost was incurred with transportation, and flight training was mixed with the work by the aircrew. However, it can be estimated that it cost anywhere from $500,000 to $2,000,000 in out of pocket money and it all came out of DND funds.

Even though this project went smoothly and no spill or accident occurred, safety measures had been put in place. Aircraft safety rules were adhered to by all participants at all times. Medically, at least one first aid kit was available at all times at the work site and procedures were laid out for medical evacuation to nursing stations or hospitals in larger communities, if need be.

Finally, EPS organized a contingency plan in case of a PCB spill situation. If such had happened, the spill would have been reported to NDHQ, DIAND, Environment Canada, and the territorial government on a priority basis based on the need for assistance, and for their knowledge so that proper responses could be given to public enquiries. A spill would have first been tackled with the local crew since it would probably have been minimal due to the fact that most individual pieces of equipment were small. If required, additional support in the form of a response crew would have been dispatched to the site by EPS. An environmental emergency 24-hour number had been provided to team leaders for that eventuality.

This cleanup operation was completed three weeks ahead of schedule. This early completion was due to good weather, lesser site contamination than expected, the large carrying capacity of the CC-115 combined with fair quality of runways at most sites, and finally, good efficient work by the cleanup crew. Any changes in any one of these conditions would have meant a longer cleanup period. The scope of work for this operation involved only a preliminary cleanup. As a result, all PCBs were removed, all visible contaminants were inventoried, and most of the abandoned POL burned. The scope of work was realistic in view of the arctic location and limited site information available. Any increase in the scope such as excavating large quantities of soil would have meant a restructuring of the concept of operation with an increase in time, manpower and equipment. The results of the soil testing and site inspections carried out by EPS will allow them to evaluate the level of residual contamination existing at those locations and prepare a report outlining the steps to be undertaken to complete the cleanup in future years. As agreed between the three departments, DIAND will be responsible for any decontamination work required after this operation.

Annex A - Site Cleanup Breakdown

ANNEX A

SITE CLEANUP BREAKDOWN

WESTERN TEAM

Station	Name/Location	Latitude	Longitude	Period of Cleanup (1985)
BAR-B	Stokes Point, Yukon	69 20' N	138 45' W	18 Jul
BAR-C	Tununuk, NWT	69 01' N	134 40' W	20, 22 Jul
BAR-D	Atkinson Point, NWT	59 56' N	131 25' W	23, 24 Jul
PIN-A	Pearce Point, NWT	69 48' N	122 40' W	29, 30 Jul, 1 Aug
BAR-E	Horton River, NWT	70 01' N	126 57' W	31 Jul, 1 Aug
PIN-B	Clifton Point, NWT	69 14' N	118 36' W	2 Aug
PIN-C	Bernard Point, NWT	68 47' N	114 50' W	5 Aug
PIN-E	Cape Peel, NWT	69 03' N	107 19' W	7 Aug
PIN-D	Ross Point, NWT	68 26' N	111 08' W	8, 9 Aug
CAM-B	Hat Island, NWT	68 19' N	100 04' W	10 to 11 Aug
CAM-A	Sturt Point, NWT	68 48' N	103 20' W	11 Aug
CAM-C	Matheson Point, NWT	68 49' N	95 17' W	12 Aug

EASTERN TEAM

Station	Name/Location	Latitude	Longitude	Period of Cleanup (1985)
FOX-E	Durban Island, NWT	67 05'50"N	62 08'07"W	18, 19 Jul
	Padloping Island, NWT	67 02'05"N	62 43'07"W	19, 20, 22, 23 Jul
FOX-D	Kivitoo, NWT	67 56' N	64 52' W	20, 24 Jul
FOX-C	Ekalugad Fiord, NWT	68 44' N	68 36' W	23, 25 to 27 Jul
FOX-B	West Baffin Island, NWT	68 37' N	73 15' W	29 Jul to 3 Aug
FOX-1	Rowley Island, NWT	69 03'30"N	79 01'37"W	30 Jul, 6, 7 Aug
FOX-A	Bray Island, NWT	69 16' N	77 21' W	30 Jul, 1 to 3 Aug
CAM-D	Simpson Lake, NWT	68 35' N	91 57' W	7, 10, 12 Aug
CAM-F	Sarcpa Lake, NWT	68 33' N	83 20' W	7, 10, 11 Aug
CAM-E	Keith Bay, NWT	68 35' N	88 08' W	10, 11, 13 Aug

REMEDIATION OF PCB CONTAMINATION IN THE KIWANIS PARK SECTION OF POTTERSBURG CREEK, LONDON, ONTARIO

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ABSTRACT

PCB contamination of the Pottersburg Creek bed sediments and flood plain soil has been identified over a distance of 5 km through the City of London. Clean-up work is underway throughout the watershed under the direction of the Ontario Ministry of the Environment. This paper focuses on the remediation work in Kiwanis Park, which is a large public park area that was of particular concern to the local residents. The paper provides an overview of the entire remediation effort, including the delineation of areas requiring remediation; the development of the strategy for remediation; the required health and safety protocols, the implementation of the remediation plan and the associated construction costs. The emphasis of the paper is on the valuable experience gained during the design and implementation of the remediation plan for the park.

INTRODUCTION

In 1980, the Ontario Ministry of the Environment (MOE) found elevated concentrations of PCBs in minnows collected from the Thames River at the mouth of Pottersburg Creek. A subsequent investigation of PCBs in the water, sediment and minnows of the creek led the MOE to industries in the Huron Street area, which were a major source of the PCB contamination in the creek. This industrial area is shown with respect to Pottersburg Creek in Figure 1. Storm water had washed PCB contaminated oil and soil from these industrial areas into storm sewers. From the sewers, PCB contaminated soil and oil were washed into the Walker Drain and Pottersburg Creek.

The sources of PCB contamination on these industrial properties have been controlled and now the more complex task of remediating Pottersburg Creek must be performed. Prior to the clean-up of the industrial properties, PCB contamination had been identified from the Walker Drain to south of Trafalgar Street, which represents approximately 5 km of the creek's length. In February 1985, CANVIRO Consultants Ltd., under contract to the MOE, initiated a program to sample and analyze the creek bed sediments and flood plain soils of Pottersburg Creek for PCB levels, delineate areas of PCB contamination and develop strategies for the remediation of these areas.

A Technical Review Committee (TRC) was convened by the MOE to provide direction regarding the selection of technically sound strategies to remediate the PCB contamination in Pottersburg Creek. The TRC has reviewed and evaluated all aspects of CANVIRO's remediation program for Pottersburg Creek to date through a series of meetings, and the committee has provided considerable

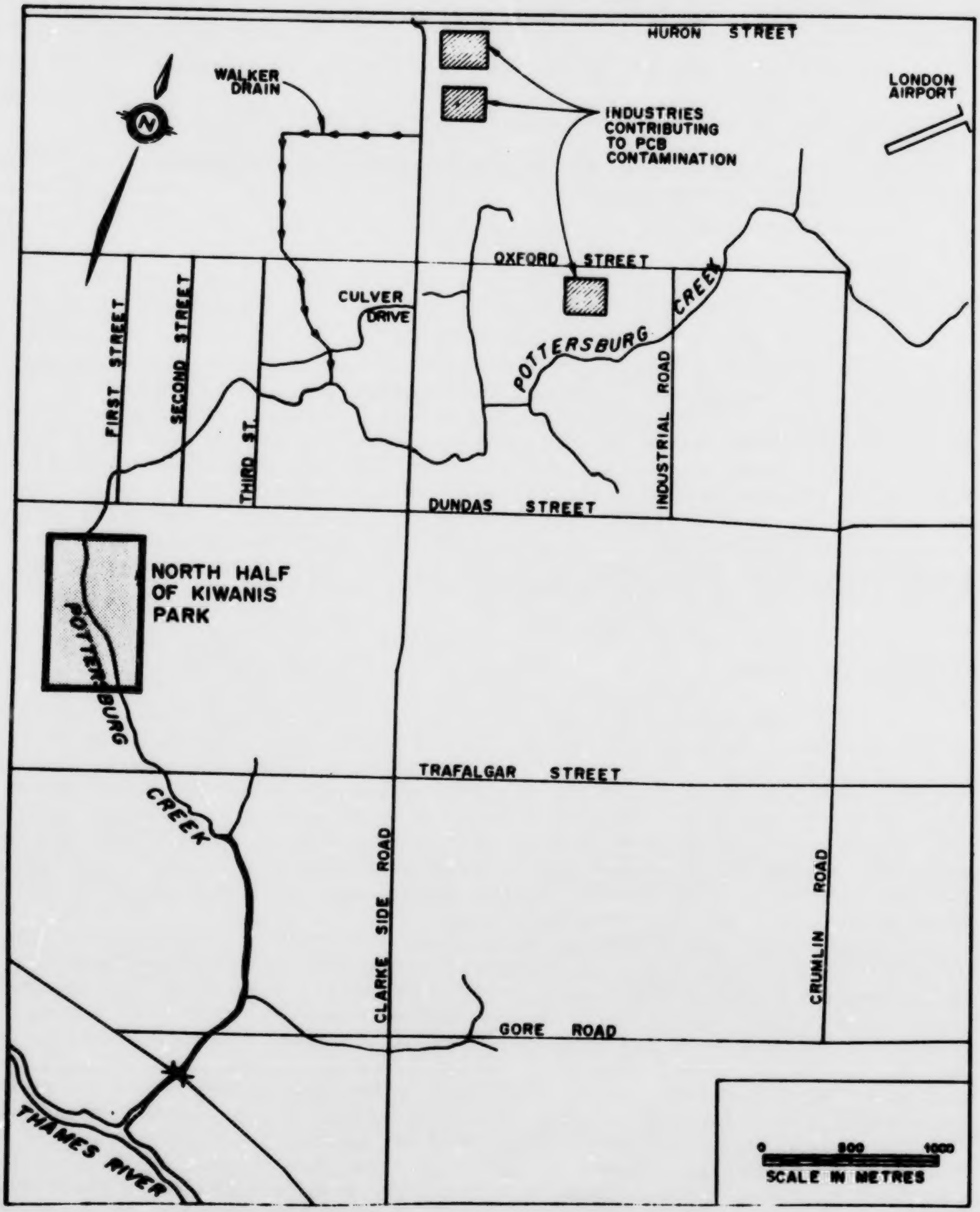
HURON STREET
WALKER DRAIN
LONDON AIRPORT
INDUSTRIES CONTRIBUTING TO PCB CONTAMINATION
OXFORD STREET
CULVER DRIVE
FIRST STREET
SECOND STREET
THIRD ST.
POTTERSBURG CREEK
INDUSTRIAL ROAD
DUNDAS STREET
NORTH HALF OF KIWANIS PARK
POTTERSBURG
TRAFALGAR STREET
CREEK
CLARKE SIDE ROAD
CRUMLIN ROAD
GORE ROAD
THAMES RIVER
0
500
1000
SCALE IN METRES

FIGURE 1. SITE PLAN OF POTTERSBURG CREEK

technical input to the remediation program. The TRC provided CANVIRO with a broad set of guidelines for remediating Pottersburg Creek based on the measured PCB contamination levels. These guidelines are shown in Table 1.

TABLE 1. REMEDIATION CRITERIA FOR POTTERSBURG CREEK

Area Type	Definition	Remediation Requirement
High PCB Contamination	Greater than 20 ppm	Remove from the site and store at secure vault
Low PCB Contamination	Generally between 1 ppm and 20 ppm	Isolate from potential contact with the public by covering with a minimum 15 cm of clean soil
Negligible PCB Contamination	Generally less than 1 ppm	No action required

Generally, a waste containing more than 50 ppm total PCBs would be designated as a high PCB waste under the hazardous waste definition. However, the TRC concluded that based on the combined effects of typical analytical errors, the quantification problems that arise from trying to "fingerprint" non-homogeneous Aroclors that have been exposed to environmental degradation and the typical sample characteristics (i.e. large range of particle size, organic content, oil content, etc.), it was possible (but not probable) for some samples to exhibit PCB concentrations which varied from 20 ppm to 50 ppm during replicate analysis. Consequently, to ensure that all potentially high PCB material was identified and handled properly and to maximize public safety, any soil or sediment with a total PCB concentration of 20 ppm or greater was designated as a "high" PCB material for the purpose of this study. The majority of the samples with greater than 20 ppm PCB concentration occurred immediately downstream from the Walker Drain.

The guidelines provided in Table 1 and the PCB data obtained as part of the remediation effort were used by CANVIRO to subdivide the Pottersburg watershed into smaller areas or creek segments, so that the varying remediation requirements along the creek could be more readily addressed. These remediation areas were prioritized for clean-up based on the PCB contamination levels, as defined in Table 1, and the public access or usage of each area. In June, 1985 Kiwanis Park was selected as one of the first areas to be remediated because it is an area of high public usage and as such, it was of particular concern to the local residents.

Work in 1985 was restricted to the North Half of Kiwanis Park, as outlined in Figure 1, due to the limited time available before the start of the winter season. This paper describes the remediation of the North Half of Kiwanis Park, which was performed as planned in September, October and November of 1985.

THE PARK SETTING

A site plan of the North Half of Kiwanis Park is presented in Figure 2. The park extends approximately 585 m north of Brydges Street, and the southern limit of work for the 1985 remediation effort was approximately 335 m south of Brydges Street. In this area the park width ranges between 100 m and 300 m. Pottersburg Creek flows from north to south through the park.

Prior to remediation, park maintenance was, for the most part, restricted to the care of the grassed areas and the clean-up of park debris. The creek had been allowed to meander, and large willows had grown along the creek banks. Due to the changing course of the creek, many of the willows encroached the creek, reducing the creek flow rates through the area and causing local pockets of significant erosion and sedimentation. Gabion baskets and rip rap had only been installed in areas where significant creek bank erosion had occurred.

The creek flood plain, which constitutes a large portion of the park, was characterized by large willow trees and young, recently planted maple trees. The park was poorly drained, with standing water often occurring in low-lying areas after rain storms. Spring runoff each year caused the creek to overflow its banks, and typically the area remained flooded for several weeks.

The park contains two areas of higher usage which were of particular concern with regard to the PCB contamination. The play area on the west side of the creek at the north end of the park contains a wading pool, several play structures (swings, see-saws, etc.) and benches, which are particularly used during the summer months. The second area of concern was at the footbridge near the southern limit of work for 1985. School children use this footbridge when travelling to and from Prince Charles School, which is shown in Figure 2. The southern limit of work was chosen specifically to include this area because of the footbridge and a zone of furan contamination immediately to the east of this footbridge, which is described in the subsequent section.

DETERMINATION OF THE SCOPE AND EXTENT OF THE REMEDIATION EFFORT

The PCB data for the North Half of Kiwanis Park are provided in Table 2. These data indicate that the North Half of Kiwanis Park was well within classification of a Low PCB Contamination Area, in that PCB contamination levels greater than 20 ppm were not detected. In fact, 43 percent of the soil and sediment samples were found to have less than 1 ppm PCB contamination, which according to the remediation criteria (Table 1) is negligible PCB contamination. Only 8 percent of the samples had PCB contamination levels greater than 10 ppm. Thus removal of the PCB contaminated soils and sediments from Kiwanis Park did not warrant consideration. The park was classified as a Low PCB Contamination Area, and as such a minimum of 15 cm of clean topsoil had to be placed over all areas of PCB contamination as a protective cap to isolate the public from this contamination.

Because dioxins and furans are often found in trace amounts in PCB spill areas, several of the soil and creek bed sediments were also tested for dioxins/furans. Three isolated areas were identified in which dioxin/furan concentrations exceeded 1 ppb, as shown in Figure 2. The action levels for removal to a secure vault on other remediation projects for dioxins and furans

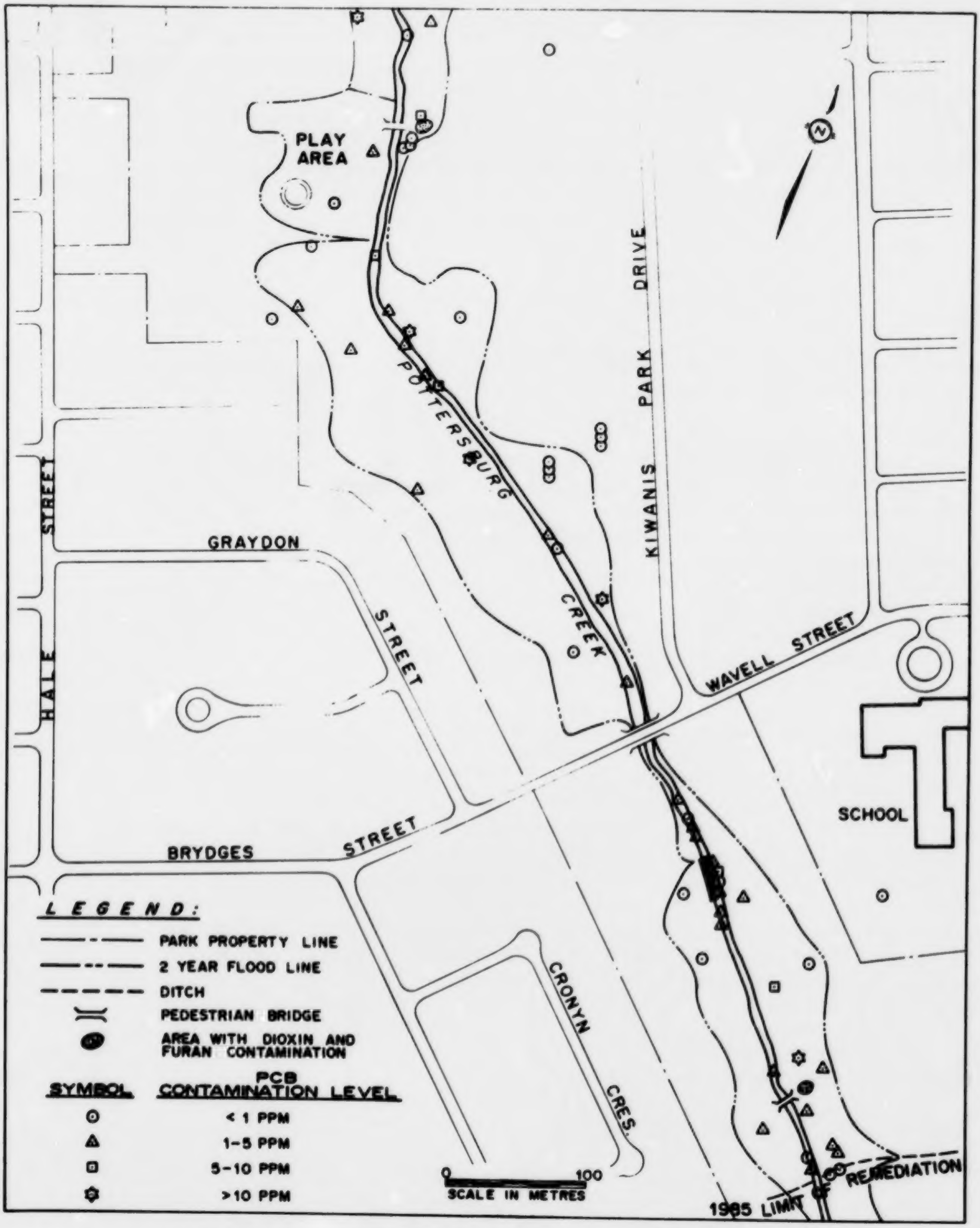
PLAY AREA
POTTERSBURG CREEK
KIWANIS PARK DRIVE
HALE STREET
GRAYDON STREET
WAVELL STREET
BRYDGES STREET
CRONYN CRES.
SCHOOL
1985 LIMIT OF REMEDIATION
N
LEGEND:
PARK PROPERTY LINE
2 YEAR FLOOD LINE
DITCH
PEDESTRIAN BRIDGE
AREA WITH DIOXIN AND FURAN CONTAMINATION
SYMBOL
PCB CONTAMINATION LEVEL
⊙ < 1 PPM
△ 1-5 PPM
▣ 5-10 PPM
✡ >10 PPM
0
100
SCALE IN METRES

FIGURE 2. SITE PLAN OF THE NORTH HALF OF KIWANIS PARK

TABLE 2. PCB CONTAMINATION LEVELS IN THE NORTH HALF OF KIWANIS PARK

PCB Contamination Range (ppm)	Number Of Measurements			
	Creek Bed	Flood Plain	Subsurface	Total
>20	-	-	-	-
15-20	-	1	-	1
10-15	-	4	-	4
5-10	3	2	-	5
1-5	14	10	1	25
<1	6	14	6	26
	23	31	7	61

have been in the range of 1 to 2 ppb, and the local residents were particularly concerned about the dioxin and furan contamination in the park. Thus, it was decided to excavate and remove the soils/sediments in all three areas of concern.

The key issue with regard to the remediation design was the distance to which the topsoil cap had to extend from the creek banks in order to encompass the PCB contamination. While PCB contamination levels generally decreased with distance from the creek, the data did not indicate an obvious distance versus contamination level relationship in the immediate vicinity of the creek. This may be due to the fact that sedimentation during flood events had occurred preferentially in certain areas which were consequently characterized by higher PCB contamination levels. Additionally, the process of PCB contamination of the flood plain would have had a significant random component, as only a small portion of the sediments deposited on the flood plain would have been contaminated with PCBs.

Since it was impossible to sample all locations for PCB contamination, a physically-based action line was required to coarsely delineate areas of potential PCB contamination from those areas that were not anticipated to be contaminated with PCBs. Creek flooding had been identified as the mechanism by which the areas adjacent to the creek were contaminated with PCBs. Thus the one, two, five , and ten year flood lines were superimposed on a map showing the PCB data to determine the suitability of these lines for use as remedial action lines. The two year flood line, as shown in Figure 2, was selected because it was the narrowest flood line that encompassed all sample locations with PCB contamination levels greater than 1 ppm. Thus all areas encompassed by the two year flood line were recommended for capping with a minimum of 15 cm of clean topsoil.

REMEDIATION PLAN AND IMPLEMENTATION

It was recognized that the park's appearance after remediation would be a significant factor in the public's acceptance of the remediation design. The local residents considered the park to be an integral component of their community, and they were uneasy about the effects that the remediation effort would have on the park's appearance. Justifiably, the local residents did not want to have their parklands adversely affected as a result of PCB contamination that they did not cause to occur. As a consequence, the preservation of trees and park structures (e.g. swing sets, benches, pathways) was integrated into the park remediation design to ensure that the use and enjoyment of these aspects of the park would not be impaired by the remediation effort. Additionally, several park improvements were identified that could be incorporated into the remediation design at minimal cost. These park improvements were included in the remediation design to restore the park to "better than original conditions".

Key aspects of the remediation plan as implemented in Kiwanis Park are outlined below. The discussions address the treatment of potentially contaminated areas that could not be effectively capped with clean topsoil, the steps taken to preserve the park trees and the remediation details to accommodate the existing park structures. The efforts made to improve the appearance and use of the park are then highlighted.

Key Aspects Of The Remediation Effort

Dioxin and Furan Contaminated Areas - Since the three areas of dioxin and furan contamination were the only areas deemed to require removal from the park area and storage at a secure vault, this effort was the first to be completed. This work was included in a related Ministry of the Environment effort to remediate the more highly PCB contaminated areas along Pottersburg Creek. A secure vault was constructed for the cleanup of the more highly PCB contaminated areas, and the contractor performing the work was trained in the stringent health and safety protocols warranted for the remediation of High PCB Contaminated Areas. By removing these three areas of dioxin and furan contamination prior to the PCB remediation work, it was possible to perform the PCB remediation work under less costly health and safety protocols for Low PCB Contaminated Areas.

Creek Banks and Sediments - The creek banks and creek bed sediments posed a problem, in that they could not be effectively capped with clean topsoil. Based on the design approach of defining the two year flood line as the remediation action line, these sediments and soils had to be considered to be contaminated with PCBs. Thus, excavation was required for the potentially contaminated creek banks and sediments. However, removal from the site and storage in a secure vault was not required, as the PCB data indicated that the creek banks and sediments were no more contaminated than the flood plain soils which were to be capped with topsoil. The excavated creek banks and sediments were therefore spread in a thin layer over the two year flood plain prior to the installation of the 15 cm topsoil cap. The volumes of sediments and soils excavated resulted in a layer of material that was less than 2 cm thick.

Due to the flow velocities in Pottersburg Creek, the creek bed sediments were sparse and generally on the order of only 5 to 10 cm thick. The affected areas were enclosed with temporary sandbag walls and dewatered, to prevent entrainment of the sediments during the excavation operation. The creek banks were excavated to depths of between 15 and 20 cm, to distances of approximately 3 m back from the edges of the creek banks. Where rip rap had been used to stabilize the banks, the rip rap were buried in shallow pits under the two year flood plain, rather than attempting to remove the potentially contaminated soils that were adhering to the stones. Because of the high flow velocities in the creek, the creek banks were capped with a 30 cm thick layer of new rip rap stone rather than 15 cm of topsoil. In a few selected erosion-prone areas such as creek bends, gabion baskets were installed along the creek banks instead of rip rap so that the topsoil cap could be better protected.

Trees Adjacent to the Creek Banks - Most of the trees growing adjacent to the creek had exposed roots as a result of creek bank erosion. The soils bound by these roots were hand excavated and spread over the two year flood plain with the excavated creek banks and sediments prior to the installation of the 15 cm topsoil cap. Rip rap was then placed on top of these roots to provide a protective barrier in the event that the roots are significantly contaminated with PCBs. Where trees had encroached on the creek, it was not possible to cover the tree roots with rip rap. In all such cases, these trees were hindering creek flows, and the resultant eddies in the creek were causing localized zones of accelerated creek bank erosion and sediment deposition. Tree and stump removal was determined to be the only effective approach to protecting the public from any PCB contamination on the roots of these trees, and in fact, removing the trees improved the alignment of the creek and reduced the rate of erosion in these areas. A total of 15 trees were removed. Due to the large number of trees remaining in the park, these removals resulted in a minimal change to the overall park appearance.

The removed trees were deemed to be uncontaminated and were disposed off-site, however, the root systems and the lowermost portions of the tree trunks were buried in shallow pits below the two year flood plain, as were the excavated rip rap stones. Burial of the tree roots and existing rip rap and other potentially contaminated items, such as debris removed from the creek bed, within the two year flood plain (which has later capped) provided a method of on-site disposal for potentially contaminated materials that otherwise would have required off-site disposal at a secure vault.

Trees on Flood Plain - Each tree on the flood plain was evaluated with regard to the tree's tolerance to the placement of the 15 cm topsoil cap over its roots and against the base of its trunk. Additionally, consideration was given to the maximum size of bulldozer that could be driven over the tree's root system without causing root damage. For the most part, the large trees (predominately willows) on the flood plain (approximately 125 trees) were deemed to be able to withstand the additional soil cover. The exceptions were the trees that were located in natural drainage swales, as a topsoil cap would have remained saturated in these areas for excessive periods of time and thus reduced root aeration. In these instances, a drainage system was required in addition to the topsoil cap. Therefore, drainage tile was first installed in swale areas with trees along the length of the swale, with the outlet at the creek bank. Gravel was placed over the drainage tile to aid the drainage process and reduce the potential for soil particles to block the drainage holes in the tile. The topsoil cap was then installed over the gravel bed.

Small trees with trunks less than 10 cm in diameter (predominantly maples, approximately 50 trees) were deemed to be unable to withstand the 15 cm of topsoil cap. In order to accommodate the 15 cm topsoil cap, these trees were raised 15 cm by removing them with a tree spade and transplanting them adjacent to their original locations, 15 cm above the existing grade. The exposed grass and topsoil on the tops of the root balls of the transplanted trees were removed to permit partial coverage with new topsoil. Thus by raising the small trees 15 cm and removing the surficial grass and topsoil, it was possible to install the 15 cm topsoil cap up to the transplanted trees and provide some coverage to the tree rootballs.

Park Structures - It was necessary to consider the park structures individually in developing the remediation plan. Structures that could be raised, such as swing sets and see-saws, were removed and installed 15 cm above existing grade. Concrete structures, such as the wading pool, could not be raised. In these instances, 15 cm of topsoil was first removed along the perimeters of these structures and spread over the two year flood plain with the potentially contaminated creek bed sediments and bank soils. This permitted the installation of 15 cm of new topsoil up to the structure, without changing the ground surface elevation adjacent to the structure. A third general category of park structures was the asphalt and gravel pathways. Within the limits of the two year flood plain, asphalt and gravel pathways were essentially reconstructed 15 cm higher than the existing grade to conform with the 15 cm topsoil cap.

Flood Plain Restoration - The activities outlined above comprise the preparatory steps that were required before installation of the 15 cm topsoil cap. Work began at the northern end of the park, and proceeded in a southerly, downstream direction to the 1985 Limit of Remediation (see Figure 2). The topsoil cap was installed as areas were prepared in order to minimize the size of the flood plain area with exposed potentially contaminated creek bed sediments and bank soils. Either hydroseed or new sod was installed on top of the topsoil cap, depending on the anticipated level of usage of the area of concern (high usage areas were sodded) and the time of year (hydroseed was not installed after October 15).

Park Improvements Included In The Remediation Effort

As discussed above, park improvements that could be easily and cost-effectively integrated into the remediation plan were performed to ensure that the park was remediated to "better than original conditions". Examples of the park improvements are as follows:

Low-Lying Areas - Several depressions and low-lying areas were located in Kiwanis Park that retained water for periods of weeks after heavy rainfall events. These low-lying areas were eliminated to provide positive drainage throughout the park by implementing one or more of the following corrective actions:

- recontour the low-lying area prior to installation of the topsoil cap
- construct a swale to drain the low-lying area to the creek prior to installation of the topsoil cap
- place greater thicknesses of potentially contaminated soils and sediments in the low-lying area prior to installation of the topsoil cap
- place more than 15 cm of clean topsoil in the low-lying area

A catchbasin and drainage pipe system was installed in a particularly large low-lying area in the high-usage play area.

Creek Banks - As previously discussed, rip rap or gabion baskets were installed along the entire length of the creek to aid in erosion protection. Also, problem trees were removed to improve the flow characteristics of the creek.

Additional/Improved Pathways - In areas where the Public Utilities Commission of the City of London planned to install new pathways in the park, the gravel base for the pathway was installed as part of the remediation work to reduce the need for future excavations in the remediated areas.

Miscellaneous Improvements
- damaged storm drains were repaired
- dead tree limbs were removed
- discarded tires and other debris were removed from the creek bed.

HEALTH AND SAFETY PLAN

A health and safety plan was required for the remediation of Kiwanis Park to protect the construction workers from the potentially contaminated soils and to prevent the contamination of areas outside the two year flood plain. Careful consideration was given to ensure that the health and safety plan was in line with the levels of PCB contamination observed. An overly conservative health and safety plan would have increased the costs for the remediation effort, and it might have unduly alarmed local residents who had used the park in the past. Thus, it was essential for the health and safety plan developed for the remediation of Kiwanis Park to "fit" the levels of PCB contamination observed.

The health and safety plan was keyed to two defined areas. These were:

1. the work area, which included all lands used by the contractor during the remediation effort, and

2. the excavation area, which was the sub-area of the work area where excavated, potentially contaminated soils were being, or had been, spread across the flood plain and had not yet been covered with clean topsoil.

The work area was delineated by temporary snow fence, which was installed to restrict access by the public into the remediation area. Signs were posted around this snow fence perimeter to warn the public that the area was a PCB clean-up zone and to tell the public to keep out of the area. A security firm was retained to watch over the work area during non-working hours to ensure that the public was in fact obeying the warning signs.

The excavation area was delineated with yellow "caution" tape supported by fence posts. The contractor was encouraged to cover potentially contaminated soils/sediments with clean topsoil as soon as possible after the potentially contaminated soils/sediments had been spread over the flood plain, thus minimizing the size of the excavation area. The excavation area was relocated as remediation proceeded along the creek.

The construction workers were required to wear protective equipment in the excavation area only, as this was the only area where they could come in contact with potentially contaminated soils/sediments. Workers were required to wear rubber boots, disposable coveralls, gloves and hard hats. The contractor supplied a change truck that had an enclosed payload with standing room at the edge of the excavation area, for the workers to change into and out of their protective equipment. Used coveralls were disposed in a metal drum if they were significantly soiled. Alternatively the coveralls were hung on hooks if they were suitable for reuse. The drums of discarded coveralls were transported to the secure vault mentioned earlier at the end of the contract for storage.

The movement of equipment, such as hand tools and heavy machinery, out of the excavation area was also closely monitored. Before equipment was removed from the excavation area, the contractor was required to thoroughly wash the equipment with water on the edge of the excavation area. In this way the transport of potentially contaminated materials outside of the excavation area was prevented.

After changing out of the protective equipment at the edge of the excavation area, the construction workers were transported to the wash-up trailer. The workers were not allowed to eat, drink or smoke inside the work area, and the wash-up trailer was positioned near the exit from the work area, to ensure that the workers always washed up before leaving the work area at the end of the day or to eat, drink or smoke. The workers were required to thoroughly wash all parts of their bodies not covered by protective equipment, namely their faces and necks, as well as their hands.

The washwaters were retained in a holding tank and tested for PCB levels as significant volumes of water accumulated. In all cases the washwaters were found to have significantly less than the MOE Interim Maximum Allowable Limit for PCBs in drinking water of 3 ppb, and as such the waters were discharged to a nearby sanitary sewer.

The above information was provided each worker on his first day on the job site in the form of a health and safety training session. Follow-up instructions and reminders were provided to the workers as required. The health and safety plan was approved during the design phase of the remediation effort by the Ministry of Labour for use in Kiwanis Park.

REMEDIATION COSTS

The construction costs to remediate the PCB contamination in the North Half of Kiwanis Park as described above are summarized in Table 3. The data show that the costs to supply and install the topsoil and sod/hydroseed were the most significant remediation costs. The cost of these two items of $262,000 represented 69% of the total remediation cost of $380,000. Also, note the small relative costs of park improvements such as ensuring positive drainage ($7,000, or 1.8 percent of the remediation cost).

CONCLUSIONS

The remediation work for the North Half of Kiwanis Park demonstrates an effective method for remediating large areas with low PCB contamination levels, without off-site disposal of large quantities of contaminated materials. In Kiwanis Park, essentially all of the contaminated materials were isolated from public contact beneath 15 cm of clean topsoil. The 71,000 square meters in the north half of the park were remediated to better-than-original conditions for a total construction cost of $380,000. Health and safety protocols

TABLE 3. COST BREAKDOWN FOR THE REMEDIATION OF THE PCB CONTAMINATION IN THE NORTH HALF OF KIWANIS PARK

Remediation Item	Cost
Mobilize, including the supply of all health and safety equipment and installation of security fence	\$ 24,000
Excavate creek bed sediments and creek banks, and remediate trees along the creek	21,000
Supply and install rip rap and gabion baskets	31,000
Transplant 50 trees and raise walkways and park structures	18,000
Construct swales and install a drainage system in a low-lying area to provide positive drainage	7,000
Supply and install 15 cm of new topsoil over 71,000 m^2 of flood plain	174,000
Supply and install sod and hydroseed over 71,000 m^2 of flood plain	88,000
Security guard for 1,300 hours	10,000
Demobilize, restore site and remove security fence	7,000
TOTAL	\$ 380,000

were implemented that both protected workers from the contaminated materials and prevented the contamination of areas outside the designated remediation area.

The most important evaluation criteria for the success of the remediation work in Kiwanis Park will be the PCB contamination levels in the park after remediation. Post-remediation monitoring will be conducted in the spring of 1986 throughout the North Half of Kiwanis Park. Samples of creek sediments and flood plain soils will be tested for PCB contamination levels, to determine the success of the remediation work in terms of the degree to which PCB contamination levels have been reduced in the park.

ACKNOWLEDGMENTS

The authors thank the members of the Pottersburg Creek Technical Review Committee for their time, assistance and valuable advice on the remediation design and implementation for the North Half of Kiwanis Park. The members of the committee were (in addition to Mr. J. Bray): Mr. J. Janse (MOE), Mr. F. Durham (MOE), Mr. A.F. Johnson (MOE), Mr. D. McBain (Environment Canada), Dr. J. Roberts (NRC), Mr. A. Choma (City of London), Dr. J. Cummins (University of Western Ontario) and Mr. J. Mahon (Citizens Coalition to Maintain the Environment).

The authors gratefully acknowledge the important contributions of Mr. R. Frier of the Ontario Ministry of the Environment and Mr. T. Little and Mr. J. Pike of CANVIRO Consultants. Mr. Frier, the Ministry of the Environment's Project Coordinator, provided valuable advise and assistance based on his considerable practical experience on earth moving and erosion control projects and in the administration of large projects. Mr. Little, the CANVIRO Site Supervisor, oversaw the entire remediation effort to ensure that remediation objectives were being attained and health and safety protocols were being followed. Mr. Pike supervised the collection of the PCB data and participated in the design phase of this remediation effort.

THE ORGANISATION OF A LARGE SCALE DECONTAMINATION OPERATION

Jean Paquin

SANEXEN INTERNATIONAL INC.

Any large decontamination project raises serious logistic problems. These problems play a very important role whenever the project has to be executed in the most effective and economical way, without impairing the rapidity of action.

Whether it be a major chemical products spill in a sensitive area, the contamination of groundwater used as a drinking water source or the presence of carcinogenic substances in a working environment following a fire, the situation has such a degree of importance and urgency that enlightened decisions have to be made.

The Project manager faces several choices:

- To act immediately or to examine the problem?
- To destroy or to remove the contaminants?
- To process wastes in situ or to dispose of them elsewhere?
- To determine which measures should be taken to protect the health and safety of all individuals and workers involved?
- To hire someone or to call for tenders?

The success of the operation — as well as the costs involved — depend on the answers to these questions.

Four main points must be considered when what is seen as a major decontamination project is to be undertaken:

- Rapidity of action
- Protection of people
- Work methodology
- Necessary infrastructures.

The Project manager must first evaluate the urgency of the situation. A delay of several hours before intervention might increase the clean-up costs ten-fold in the case of an accidental spill on a water body. In the case of a land spill a 2 months delay for calls and study of tenders can also substantially increase the clean-up costs. On the other hand, any hasty measure taken without further consideration could also have serious consequences.

The next point to be taken into consideration is the one related to the protection of those workers or individuals who could be affected by the contamination, once the project is in its realization phase.

It might be tempting to set up maximum safety measures. Nevertheless such an action can prevent actually implementing the project. For example, it would be useless to protect the individuals to such an extent that the daily doses of contaminants be 1000 times lower than those they are exposed to in their current environment. On the other hand, product toxicology must be well understood, as well as ingestion patterns, according to the site characteristics. Any inability to execute a certain type of work or acute susceptibility from the part of some individuals must be considered.

Work methodology must then be defined for that is where effectiveness and costs factors are most sensitive. Clean-up of the area can be achieved by lixiviation of the contaminants, biodegradation, solvent extraction or by merely removing the contaminated soil. The best approach could consists of stopping the contamination through a chemical fixation process, or to confine the spill. Any large project must be based on an analysis of the short-term and long-term consequences of the selected options.

Depending on the decontamination process selected, a water, air or waste treatment station is normally required as soon as the project takes a magnitude that goes beyond certain proportions. In the past several clean-up operations were more costly than necessary or the individuals in charge had a very limited knowledge of the available technologies.

Finally, a zoning system should be established and strictly adhered to, according to the nature of the contaminants involved and the progress of the clean-up operation. To ignore this principle might result in a heavy penalty as far as time and costs are concerned.

The next problem deals with the infrastructures required on the site i.e. headquarters, communications, stocking area, warehouses, workers' living quarters, access control, and the equipment decontamination section. In the absence of the necessary infrastructures, the clean-up period will be much longer than necessary and might cost more.

As an example, let us consider a PCB fire within a large building.

In the case of a fire, the PCBs will form PCDFs (furanes) and possibly PCDDs (dioxines), though in lesser quantities. These products are much more toxic than the PCBs and their permissible concentration levels in a working environment are consequently very low.

In november 1984, the explosion of a capacitor bank caused the combustion of close to 600 liters of askarel and contaminated hundreds of thousands of square meters inside a building complex in Varennes, Québec.

Once the people had been evacuated and the fire extinguished, the priority was to collect and treat the water used to fight the fire.

Procedures were implemented within a few days to protect the staff and working methods were determined. These methods included vacuuming of the surfaces followed by an air treatment and the use of solvents. The installation of a still to recycle the solvent and to concentrate the residues was also initiated The clean-up operation then started in the less contaminated areas.

During the three following weeks, the necessary infrastructures were erected. A group of mobile homes or "village" was set up. It included a security station, a locker room for daily clothing, a stockroom for the safety equipment, a work clothes dressing room, an access room to enter or leave the contaminated area, shower facilities, lavatories, a dining-room and a conference room for training sessions and safety meetings.

A decontamination center was built at the same time. It included water treatment facilities, air pumping and treatment stations, the still, safety equipment cleaning facilities and a separate temporary shelter where the equipment removed from the bulding was to be decontaminated. A contaminated equipment stocking area was also set up. Later freon decontamination chambers were installed To clean a variety of additionnal equipment.

Later, the existence of a water treatment system permitted the use of a faster cleaning process, i.e. the application of a detergent foam on the surfaces to be cleaned followed by high pressure water rincing.

A zoning system and an access control system were established in order to avoid recontaminating the areas that had been cleaned and to obtain from the Quality Control Group a reclassification of these areas.

The water treatment system based on the use of detergent, combined with the safety equipment cleaning method allowing for its reuse, resulted in millions of dollars of savings.

Through the efforts of several teams on day and night shifts the first, second and third buildings were reopened respectively five, six and eleven months later.

A comparison between the clean-up operations conducted jointly by Sanivan and - in this particular case - the owner of the facilities and similar decontamination operations at other locations shows clearly how important an approach such as the one described here is.

YEARS	LOCATION	COST ($/m2)
1981	Binghampton	1400
1983	San Francisco	900
1984	Santa Fe	475
1984	Varennes	35

Several other factors also contribute to explain the above differences, such as the size and the type of construction (that lowered costs at the Varennes location), the standards to be met (higher in San Francisco) and the nature of the contamination (that lowered the costs in Santa Fe). Nevertheless, the costs of the Varennes clean-up operation would have been much higher than necessary should the process used at that location be the conventional one used elsewhere.

To sum it up, let us say that major questions must be asked in the case of a large scale decontamination operation. The answer to these questions will largely determine the efficiency and the cost of a clean-up operation.

JP/cv/DG-07

THE KEY LAKE SPILL

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INTRODUCTION

On January 5, 1984 at approximately midnight, Water Storage Reservoir No. 2 began to overtop at the Key Lake uranium mining facility in northern Saskatchewan. Despite heroic efforts by the facility employees to stop the flow, within several hours a notch approximately 1.5 metres deep had formed. By early afternoon a decision was made to cut the heavy plastic liner of Reservoir No. 2 as erosion was threatening the integrity of the adjacent even larger Reservoir No. 1. Approximately 87,000 m^3 of water was lost from the reservoirs when the flow finally ceased early in the morning on January 7. A detailed chronology of the events from January 5 to 7 is presented in Appendix A.

This paper will provide:

- a brief historical perspective of the mining facility including waste management design and surrounding terrain and environment;
- the reason(s) for the occurrence;
- a summary of the efforts to stop and minimize the environmental impact of the spill;
- the response of the media and the regulatory agencies;
- immediate environmental consequences of the spill and remedial action decisions taken; and
- an assessment of the long-term impact on the lake receiving the spill and the surrounding environment.

HISTORICAL PERSPECTIVE

The Key Lake mine is situated on the southern-mid border of the Athabasca sandstone formation in northern Saskatchewan. Within this formation are found the richest uranium deposits in the world.

The Key Lake orebody which was discovered in 1975 is contained in two relatively massive but shallow orebodies known as the Gaertner and Deilmann deposits. The average grade of the ore is 2.35 percent and reserves are estimated at approximately 70,100 tonnes both as U. In comparison, the Elliot Lake uranium deposit, although having reserves two to three times as large, is contained in hard rock, requires underground mining and grades approximately 0.1% U_3O_8.

The mine/mill site is relatively flat, composed mostly of sand and till and many small lake-filled depressions. Those lakes are drained generally to the northeast by the Geikie and Wheeler Rivers.

Typical of the sub-arctic region, vegetation is mostly jackpine and spruce which are normally small owing to the poor soil conditions and frequent forest fires.

The nearest human habitation to the site is approximately 70 km and larger towns are Uranium City, 300 km to the northwest and LaRonge, some 240 km to the south. Figure 1 shows the location of the mining facility.

After several years of site preparation, design work and an extensive environmental assessment hearing, permission to construct the facility was given by the Atomic Energy Control Board (AECB) and the Saskatchewan government. The licence to operate the facility was granted by the AECB on June 23, 1983. All agreed that this $500,000,000 facility was the ultimate "state of the art" uranium mining and milling facility in the world, particularly when one considered the systems and procedures put in place to manage and treat the wastes and protect the environment. These systems included: a crystallization plant to remove ammonia from the effluent and produce an ammonium sulphate fertilizer; two large wastewater storage reservoirs; an engineered and fully man-made tailings impoundment system; sophisticated heavy metals and radium removal circuits and effluent monitoring ponds designed such that no effluent would be released to the envirnment unless it met a series of licence imposed limits. Figure 2 shows the layout of the Key Lake facility.

CIRCUMSTANCES LEADING TO THE SPILL

New facilities, especially complex ones can always be expected to undergo start up problems and Murphy's Law is generally directly proportional to the complexity. The Key Lake facility was no exception.

Operational difficulties were encountered with the effluent treatment facilities. The inventory of contaminated water from various parts of the facility steadily increased in the two wastewater storage reservoirs. The sources of influent to the storage reservoirs are presented in Table 1.

Both reservoirs were constructed of glacial till, sand, some cobblestone and boulders, and were lined with Bentonite and high density polyethylene.

The onset of winter caused a frozen crust of snow covered ice to form on the reservoirs and it became difficult to visually determine how much freeboard was available.

During the period immediately prior to the spill, the surface and groundwater drainage from the mine was being pumped to Reservoir No. 1. This water, which is used as mill process water was not being withdrawn as the mill was down for maintenance.

Reservoir No. 1 overtopped through a design spillway into Reservoir No. 2. The remaining capacity of Reservoir No. 2 was insufficient and this reservoir overtopped.

THE SPILL

Appendix A provides a detailed chronology of events during the spill In summary, the released water flowed for about 300 m, along a road constructed near the base of the reservoir, and entered the north-east corner of Gerald Lake. Although some of this water flowed over the ice, some entered the lake, mixed with and displaced some of the lake water. This excess water followed several drainage ditches in the surrounding muskeg until it was stopped by the tailings pond road.

RESPONSE OF THE REGULATORY AGENCIES AND THE MEDIA

As required by the Regulatory Agencies, Key Lake Mining Corporation reported the spill promptly, and measures were taken to have inspectors on the scene. The response of the media was equally prompt and widespread. The event made national television news immediately and was billed as a "nuclear disaster". Extensive local, Saskatchewan, coverage was to continue for many weeks after the event. As in all events associated with the nuclear industry, highly polarized views on both sides of the issue were reported. These ranged from demands to immediately shut down operations at the facility and hold a public inquiry to statements that this event was of very minor significance. The regulatory agencies and politicians of the day naturally had these attitudes as well as the technical issues to consider.

IMMEDIATE ENVIRONMENTAL CONSEQUENCES OF THE SPILL

The spill reported to Gerald Lake where it mixed with and displaced some of the lake water. The morphometric characteristics of the lake are given in Table 2 and the depth contours are given in Figure 3. Extensive sampling of the water in the lake, displaced water and lake sediments was conducted. The results of the sampling are contained in Table 3 and Figures 4 and 5. Tables 4 and 5 contain a comparison of pre- and post-spill water quality in Gerald Lake and lake (mixed) concentrations versus Saskatchewan drinking water objectives respectively. Table 6 compares sediment contaminant levels in Gerald Lake and other lakes in the Key Lake area.

These analyses indicated that most of the contaminated water, probably due to temperature and consequently density effects, reported as a plug with limited mixing into the lake. Sediment samples also indicated that some contamination occurred in that horizon. Because of the stagnant groundwater regime in the vicinity of Gerald Lake, it was anticipated there would be little if any movement of spilled water into the groundwater.

In summary then, the majority of spill water was located in Gerald Lake at depths exceeding one meter and of the list of contaminants, only uranium and radium-226 exceeded Municipal Drinking Water Quality Objectives for Saskatchewan. If the spill water were to be mixed thoroughly within the lake, diluted with spring run-off and further diluted in the Yak and David Creek catchments, then even those levels would have been well below drinking water objectives in the Wheeler river.

REMEDIAL ACTION

After much discussion amongst the regulatory agencies, Key Lake Mining Corporation was directed by the Saskatchewan Department of the Environment to pump approximately 200,000 m^3 of the deeper "contaminated" water from Gerald Lake for use in the milling process. This action coupled with the requirement to drain the storage reservoirs resulted in a large inventory of wastewater to be accumulated in the tailings impoundment. The AECB consequently directed the Company to expand effluent treatment capacity.

The pumping was completed prior to spring breakup and the Company was required to monitor on a daily basis the runoff flow from the lake for various parameters including uranium and radium-226. Sampling indicated that most of the contaminants associated with the spill had been recovered or had been bound up in the sediments. Finally, liquid level probes were installed in both reservoirs and levels were maintained at or well below the 1.5 m freeboard required.

CURRENT STATUS IN GERALD LAKE

Following the spill the contaminants of concern settled onto the bottom sediments by a number of mechanisms. Tables 7 and 8 present a summary of sediment chemistry and water quality results for Gerald Lake for the period of

January 1984 to May 1985. Analysis of this data shows that the water in all parts of the lake met the "Saskatchewan Surface Water Quality Objectives" for all parameters.

With respect to the long term fate of the fauna and sediments, the following is a quote from reference number 2.

> "As examined and discussed by IEC Beak (March 1985; June 1985) the impact of the spill on the resident macroinvertebrate and Burbot fish communities was minimal and of short duration. In the intermediate term the after effects of the spill are expected to be generally beneficial to both communities. This relates primarily to the input of sands and gravels, which should improve the Burbot spawning habitat and to the settling out of fine silty clay material which will probably support greater densities of benthic organisms than the organic lake bottom sediments. The finding by IEC Beak (June 1984) of benthic fauna living in the freshly deposited silts and clays in the deep basin of Gerald Lake is strong evidence that the materials deposited by the spill are not toxic. In the longer term as the spill-related materials are covered over with naturally-occurring organic material the macroinvertebrate and Burbot fish communities should revert to their pre-spill status."

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4. IEC Beak Consultants Ltd. - June 1984.
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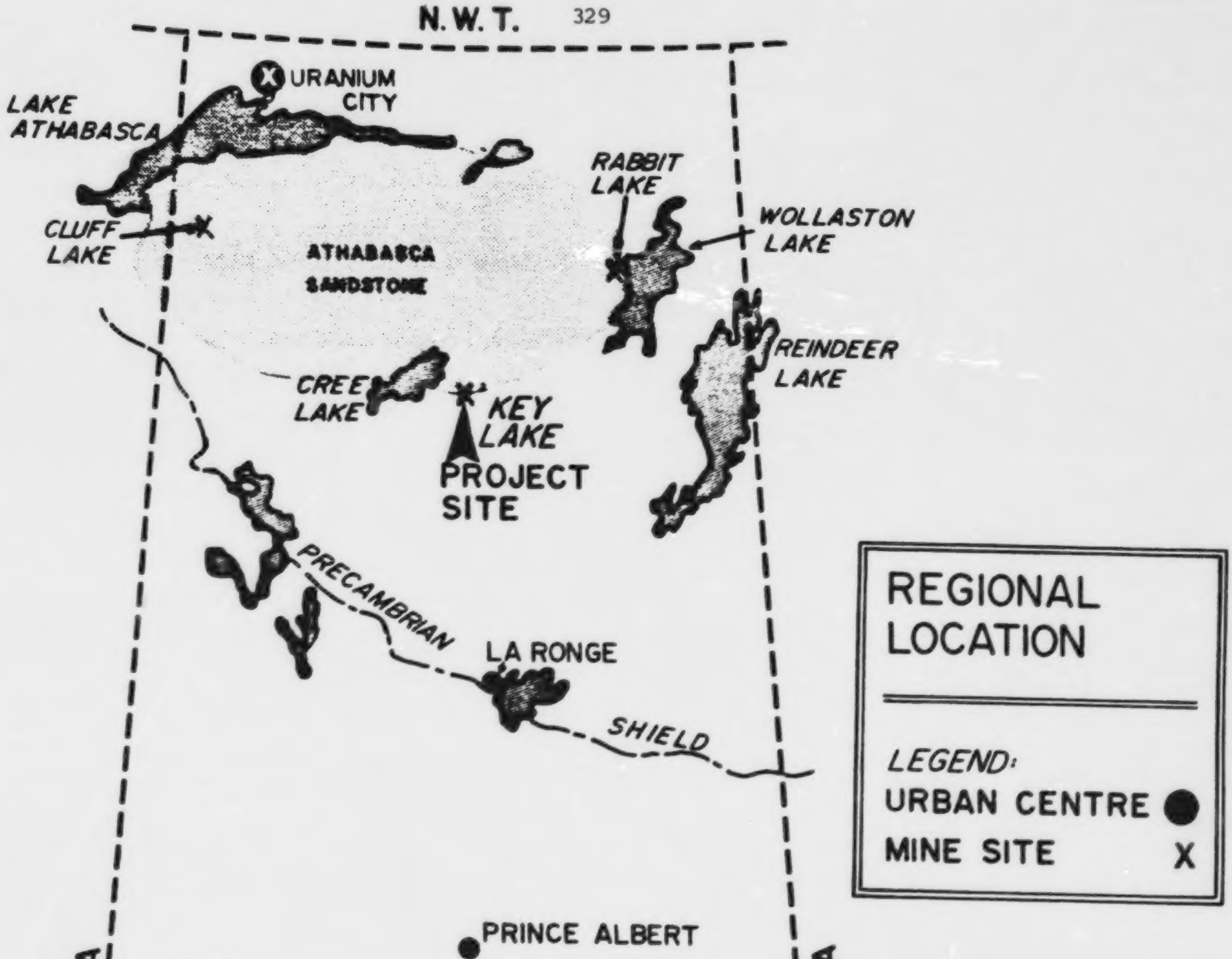
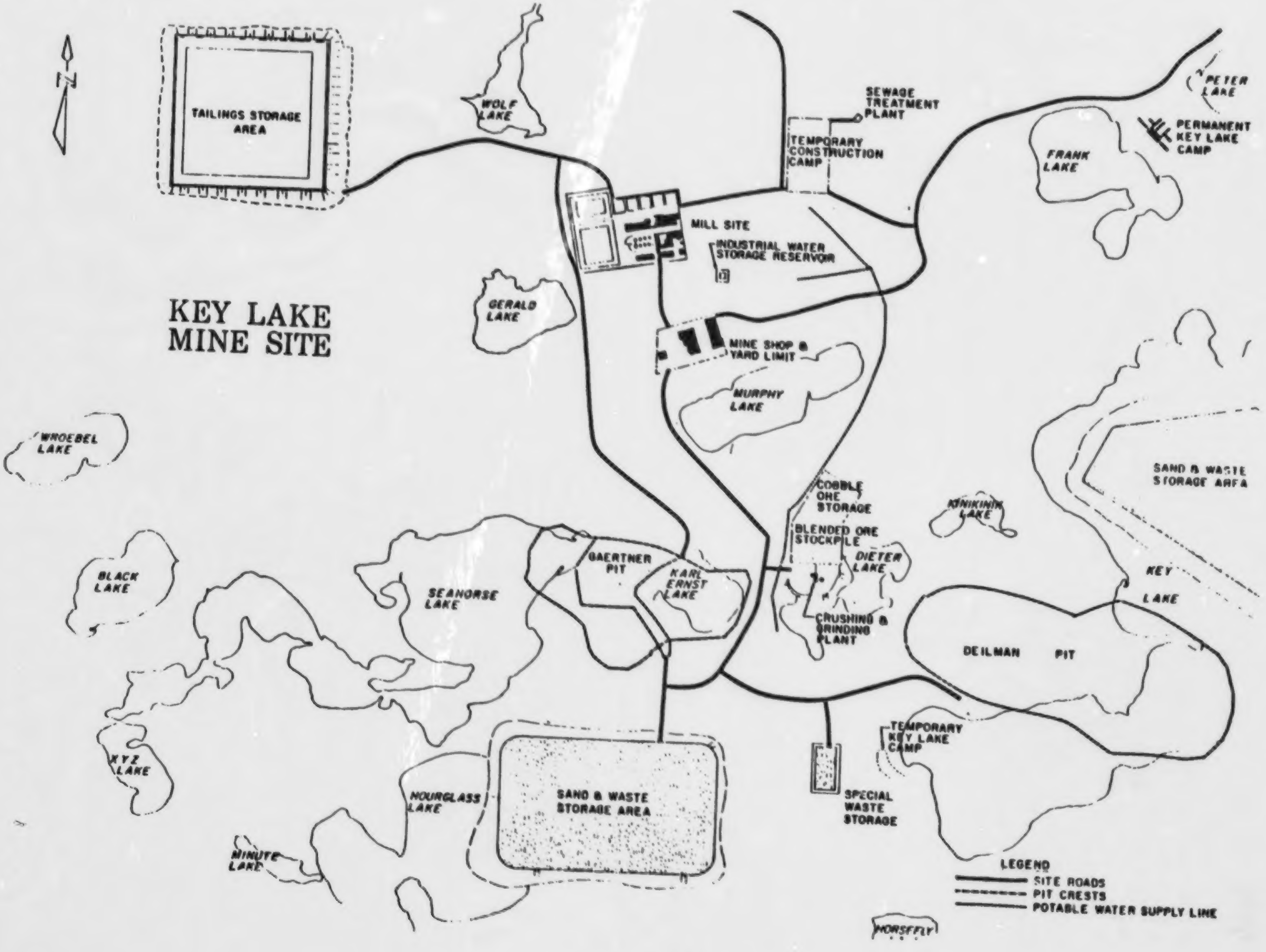

N.W.T.
URANIUM CITY
LAKE ATHABASCA
CLUFF LAKE
ATHABASCA SANDSTONE
RABBIT LAKE
WOLLASTON LAKE
REINDEER LAKE
CREE LAKE
KEY LAKE PROJECT SITE
PRECAMBRIAN SHIELD
LA RONGE
REGIONAL LOCATION
LEGEND:
URBAN CENTRE ●
MINE SITE X
PRINCE ALBERT
SASKATCHEWAN
SASKATOON
ALBERTA
MANITOBA
CANADA
REGINA
beak
CANADA
U.S.A.

FIGURE 1

Figure 2 KEY LAKE MINE SITE SHOWING MAJOR SITE FACILITIES


N
TAILINGS STORAGE AREA
WOLF LAKE
SEWAGE TREATMENT PLANT
TEMPORARY CONSTRUCTION CAMP
PETER LAKE
PERMANENT KEY LAKE CAMP
FRANK LAKE
MILL SITE
INDUSTRIAL WATER STORAGE RESERVOIR
GERALD LAKE
KEY LAKE MINE SITE
MINE SHOP & YARD LIMIT
MURPHY LAKE
WROEBEL LAKE
SAND & WASTE STORAGE AREA
COBBLE ORE STORAGE
KINIKINIK LAKE
BLENDED ORE STOCKPILE
DIETER LAKE
BLACK LAKE
SEAHORSE LAKE
GAERTNER PIT
KARL ERNST LAKE
KEY LAKE
CRUSHING & GRINDING PLANT
DEILMAN PIT
TEMPORARY KEY LAKE CAMP
XYZ LAKE
HOURGLASS LAKE
SAND & WASTE STORAGE AREA
SPECIAL WASTE STORAGE
MINUTE LAKE
LEGEND
SITE ROADS
PIT CRESTS
POTABLE WATER SUPPLY LINE
HORSEFLY

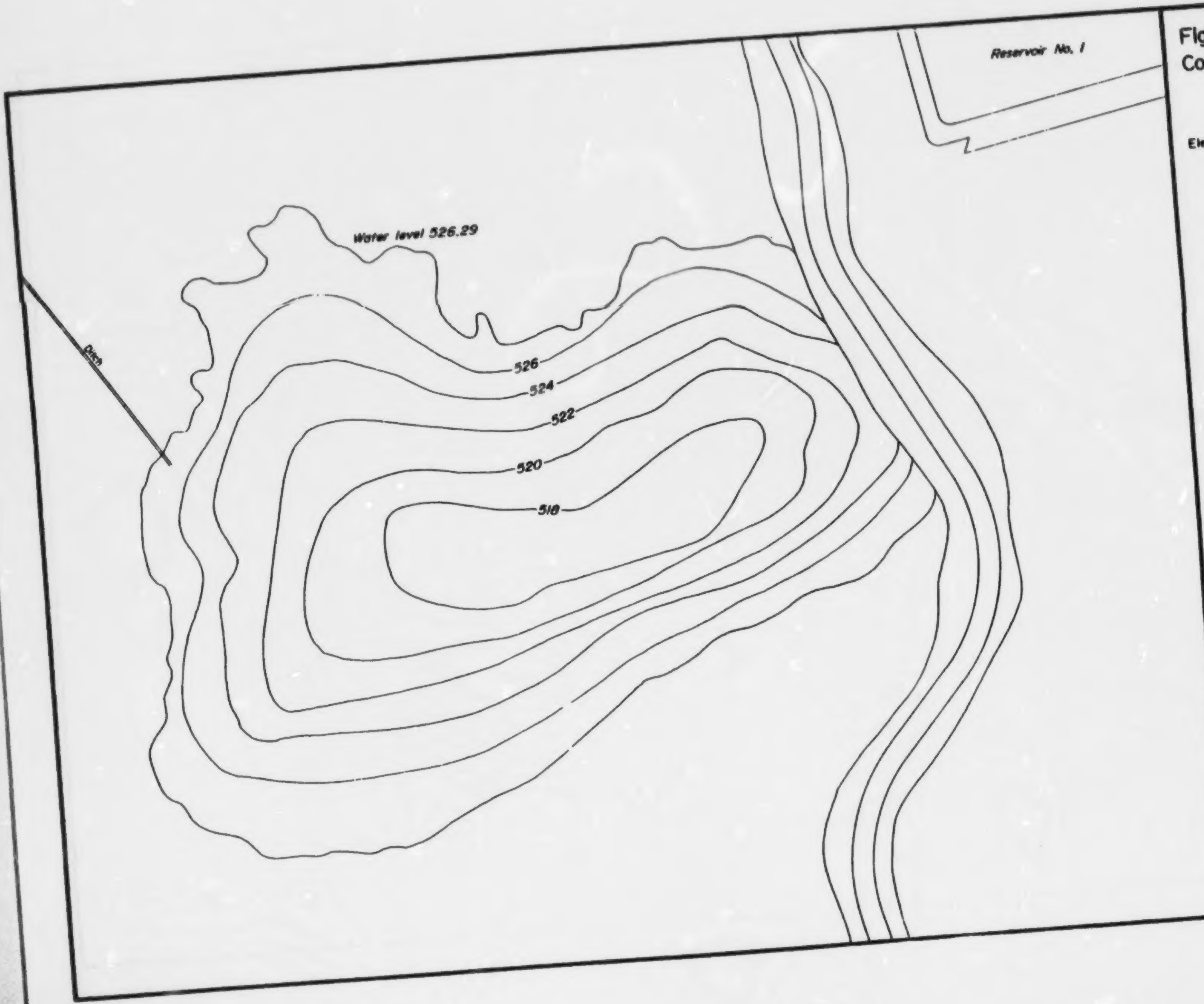
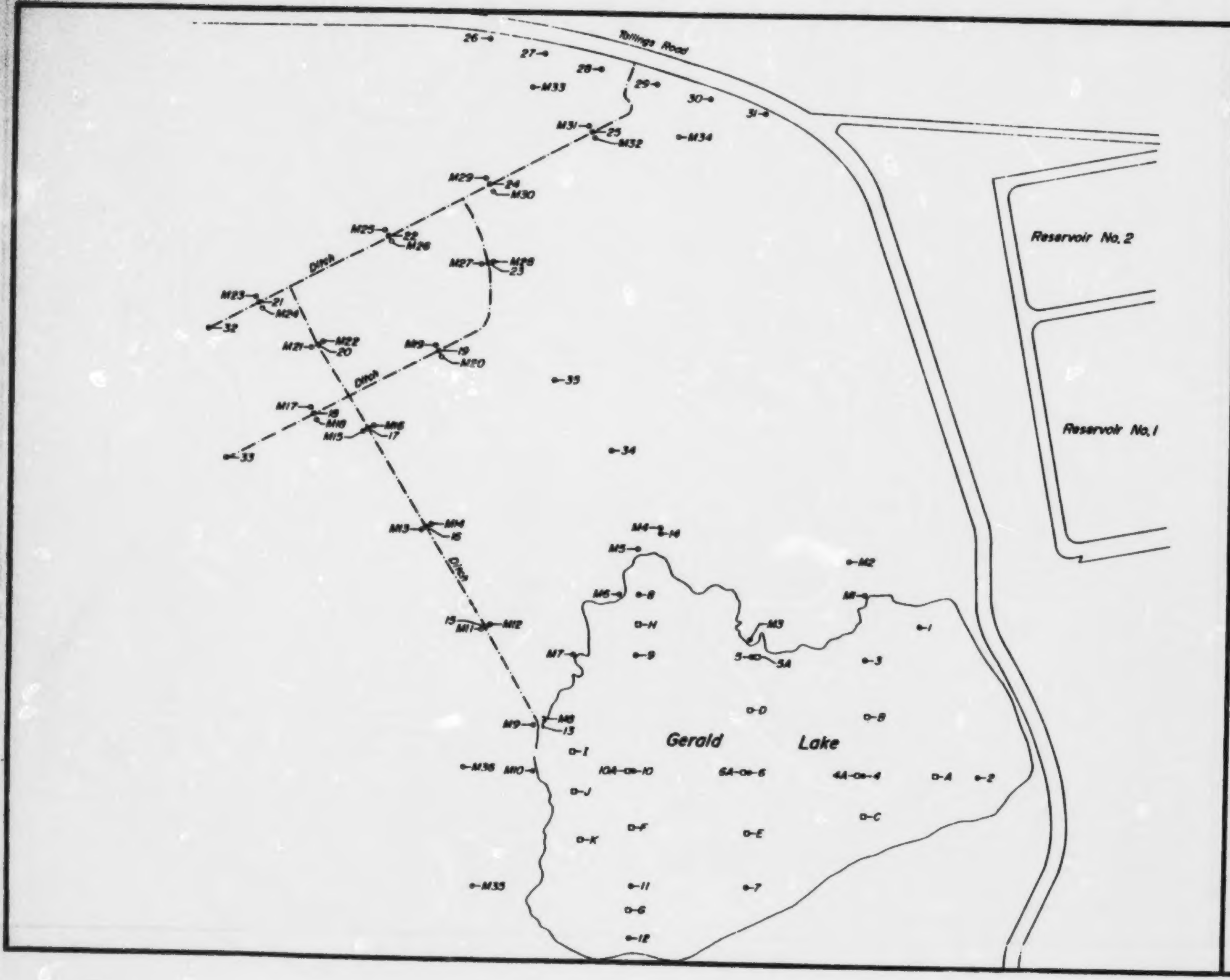

Reservoir No. 1
Water level 526.29
Ditch
526
524
522
520
518
N
0
50
100
metres

Figure 3 Depth Contours of Gerald Lake. |1|

Elevations In Metres Above Sea Level

INTEGRATED
ENVIRONMENTAL
SCIENCES INC.


Tailings Road
Reservoir No. 2
Reservoir No. 1
Gerald Lake
Ditch
26
27
28
29
30
31
M33
M34
M31
25
M32
M29
24
M30
M25
22
M26
M27
M28
23
M23
21
M24
32
M21
M22
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M19
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M17
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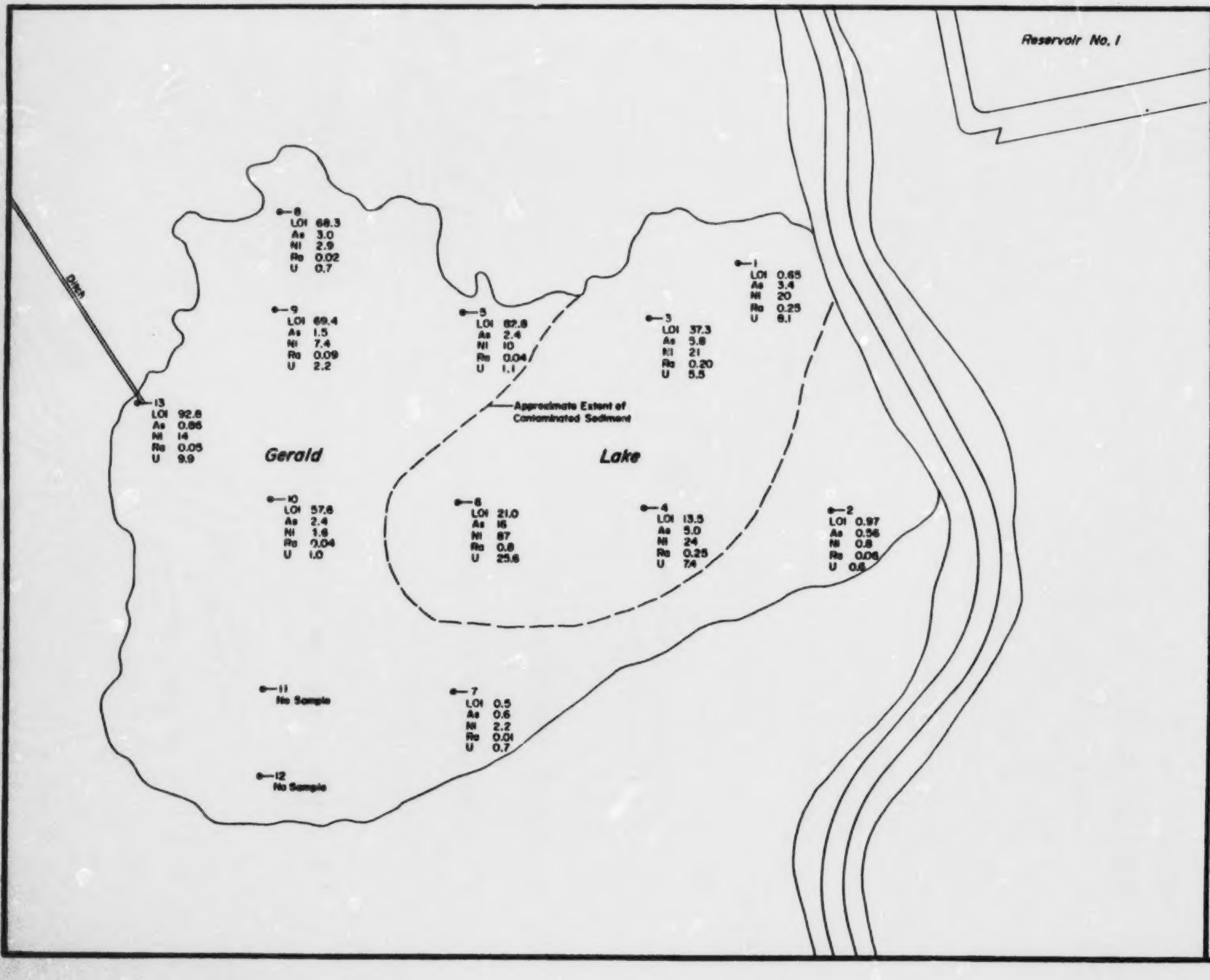
M18
M15
M16
17
33
34
M13
M14
16
M4
14
M5
M2
M6
8
M1
H
M3
1
M11
M12
15
M7
9
5
5A
3
D
B
M9
M8
13
I
M36
M10
10A
10
6A
6
4A
4
A
2
J
C
K
F
E
M35
11
7
G
12

Figure 4 Water, Sediment and Muskeg Sampling Locations. |1|

35 Water, Sediment Sample Site
M36 Muskeg Sample Site
K Sask. Environment Sample Site
N
0
100
200
metres

INTEGRATED
ENVIRONMENTAL
SCIENCES INC.



Reservoir No. I
Ditch
1
LOI 0.65
As 3.4
Ni 20
Ra 0.25
U 8.1
2
LOI 0.97
As 0.56
Ni 0.8
Ra 0.06
U 0.6
3
LOI 37.3
As 5.8
Ni 21
Ra 0.20
U 5.5
4
LOI 13.5
As 5.0
Ni 24
Ra 0.25
U 7.4
5
LOI 82.8
As 2.4
Ni 10
Ra 0.04
U 1.1
6
LOI 21.0
As 16
Ni 87
Ra 0.8
U 25.6
7
LOI 0.5
As 0.6
Ni 2.2
Ra 0.01
U 0.7
8
LOI 68.3
As 3.0
Ni 2.9
Ra 0.02
U 0.7
9
LOI 69.4
As 1.5
Ni 7.4
Ra 0.09
U 2.2
10
LOI 57.6
As 2.4
Ni 1.6
Ra 0.04
U 1.0
11
No Sample
12
No Sample
13
LOI 92.8
As 0.86
Ni 14
Ra 0.05
U 9.9
Approximate Extent of Contaminated Sediment
Gerald
Lake

Figure 5 Distribution of Spill Contaminants in Aquatic Sediments of Gerald Lake. |1|

LOI	LOSS OF IGNITION (%)
As	ARSENIC (mg/g)
Ni	NICKEL (mg/g)
Ra	RADIUM 226 (Bq/g)
U	URANIUM (mg/g)

N
0
50
100
metres

INTEGRATED
ENVIRONMENTAL
SCIENCES INC.

Table 1. Sources of Influents for Water Storage Reservoirs No. 1 and 2.[*] |1|

INFLUENT ORIGIN	COMMENTS
Reservoir No. 1	
1. Seepage from ore, cobble ore and special waste stockpile.	Highly seasonal with lowest flows during winter months
2. Run-off from crushing and grinding area.	Highly seasonal with lowest flows during winter months
3. Seepage and run-off from open pit.	Major source of water prior to and at time of spill, although total volume not known
4. Floor drainage and laboratory waste.	Thought to be of minimal input
Reservoir No. 2	
1. Supernatant and seepage recovery from tailings.	Major source of water; 15,000 m^3 of supernatant and 57000 m^3 of seepage in December 1983
2. Run-off from mill site.	Highly seasonal with lowest flows during winter months
3. Rejected water from monitoring ponds.	No water was returned to the reservoir in December 1983

[*] From KLMC (1982) and personal communication with KLMC officials.

Table 2: Morphometric Characteristics of Gerald Lake. |1|

Shore length (km) = 1.48

Mean Depth (m) = 3.53

Maximum Depth* (m) = 10

Surface Area (ha) = 9.96

Water Volume (m^3) = 350,000

Shore development = 2.65

Volume Development = 1.06

Water Level* = 526.29m

*From KLMC (1984)

Table 3: Chemical Analysis of Water Samples Collected from Gerald Lake, January 1984.* |1|

Analyte (units)	1a	2a	3a	4a	4b	4c	5a	6a	6b	6c
	Station Number (a = surface, B = mid-depth, c = bottom)**									
pH (pH units)	7.3	7.0	7.1	6.9	9.0	9.1	7.2	7.0	9.0	9.1
Specific (umhos/cm) Conductivity	85	57	48	53	435	410	30	36	447	420
Calcium (mg/l)	10	6.2	5.0	5.9	63	68	2.8	3.5	69	64
Sulphate (mg/l)	20	13.6	5.3	14.8	176	179	7	3.8	182	167
Total Suspended Solids (mg/l)	2	2	1.6	<1	12	12	<1	1.2	11	9
Ammonia (mg/l)***	0.4	0.3	0.2	0.3	8.2	2.5	0.2	0.2	9.1	2.5
Arsenic (mg/l)	<.005	<.005	<.005	<.005	.011	.021	<.005	<.005	.016	.011
Nickel (mg/l)	.02	.02	<.01	<.01	.04	.03	<.01	<.01	.04	.03
Lead (mg/l)	.004	.003	.003	.003	<.02	.003	.004	.006	<.02	.005
Uranium (ug/l)	20	<5	<5	<5	78	76	22	7	91	81
Radium-226 (Bq/l)	.08	<.02	<.02	<.02	.51	.43	.02	.04	.57	.48

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* Data provided by KLMC.

** For location see Figure 2.

*** Originally reported as NH_3 Ammonia but here converted to N, ammonia.

Table 3: Chemical Analyses of Water Samples Collected from Gerald Lake, January 1984.* |1|
(Cont.)

Analyte (units)	Station Number (a = surface, B = mid-depth, c = bottom)**									
	7a	8a	9a	10a	10b	10c	11a	11b	11c	13a
pH (pH units)	6.8	7.1	8.4	7.0	8.9	8.5	7.0	7.7	9.0	6.9
Specific (umhos/cm) Conductivity	55	34	429	40	385	325	108	299	407	33
Calcium (mg/l)	5.8	3.4	3.8	4.0	53	74	13.6	46	63	3.6
Sulphate (mg/l)	7.2	12	12.3	5.3	142	108	32.1	114	149	6
Total Suspended Solids (mg/l)	<1	8	3.6	1.6	9.4	6.8	1.2	5.2	7.6	6
Ammonia (mg/l)***	0.2	0.2	0.2	0.2	2.5	2.5	0.7	7.4	2.5	0.2
Arsenic (mg/l)	<.005	<.005	<.005	<.005	.009	.009	<.005	.009	<.005	<.005
Nickel (mg/l)	<.01	<.01	<.01	<.01	.05	.03	.02	.05	.04	<.01
Lead (mg/l)	.005	.005	.003	<.002	.002	.003	.002	<.02	.003	.003
Uranium (ug/l)	<5	17	<5	10	67	93	12	98	54	<5
Radium-226 (Bq/l)	<.02	<.02	.02	.03	.43	.52	.05	.38	.49	<.02

* Data provided by KLMC.
** For location see Figure .
*** Originally reported as NH_3 Ammonia but here converted to N, ammonia.

Table 4: A Comparison of Pre- and Post-Spill Water Quality in Gerald Lake. |1|

Analyte (unit)	Pre-Spill		Post-Spill	
	Mean (Range)	Sample Size	Mean (Range)	Sample Size
pH (pH units)	6.66 (6.20 - 6.90)	3	7.8 (6.8 - 9.1)	20
Specific Conductivity (umhos/cm)	24 (15 - 38)	3	207 (30 - 447)	20
Total Suspended Solids (mg/l)	5.0 (4.0 - 6.0)	3	5.2 (<1 - 12)	20
Sulphate (mg/l)	1.9 (<1.0 - 3.8)	3	67.8 (3.8 - 182)	20
Calcium (mg/l)	1.51 (0.71 - 2.8)	3	28.4 (2.8 - 74)	20
Total Kjeld. Nitrogen (mg/l)	0.37 (0.05 - 0.76)	3	- (-)	0
Ammonia,N (mg/l)	0.02 (N/A)	1	2.1 (0.2 - 9.1)	20
Nickel (mg/l)	0.002 (<0.001-0.005)	3	0.02 (<0.01-0.05)	20
Lead (mg/l)	0.004 (0.003 - 0.004)	3	0.006 (<0.002 - <0.02)	20
Arsenic (ug/l)	<0.5 (<0.5)	3	7.6 (<5 - 21)	20
Uranium (ug/l)	<0.5 (<0.5)	3	38 (<5 - 98)	20
Radium-226 (Bq/l)	0.041 (<0.004 - 0.1)	3	0.21 (<0.02 - 0.57)	20
Lead-210 (Bq/l)	0.068 (<0.004 - 0.1)	3	- (-)	0
Polonium-210 (Bq/l)	0.075 (<0.004 - 0.2)	3	- (-)	0
Thorium-230 (Bq/l)	<0.03 (N/A)	1	- (-)	0

Table 5: Gerald Lake (Mixed) Contaminant Concentrations versus Saskatchewan Drinking Water Objectives. |1|

	Gerald Lake[1]	Drinking Water Objectives[2]	Water Quality Objectives[3]
Sulphate	117	500	n.s.
Ammonia	3.6	n.s.	1.0*
Arsenic	10.5	50	10
Lead	0.008	0.05	0.05
Nickel	0.03	n.s.	n.s.
Radium - 226 (Bq/l)	0.37	0.10	0.10
Uranium (ug/l)	62	20	n.s.

1. A calculated value assuming complete mixing in Gerald Lake.
2. Municipal Drinking Water Quality Objectives (Saskatchewan Environment 1980).
3. Water Quality Objectives (Saskatchewan Environment 1975).

* For total nitrogen

Table 6 A Comparison of Analytical Results of Spill Contaminants in Aquatic Sediments from Gerald Lake and the Key Lake Area.[1]

	Gerald Lake Background*	Gerald Lake Spill Influenced**	Key Lake Area***
Nickel (ug/g)	0.8 - 14	20 - 87	43 - 228
Arsenic (ug/g)	0.56 - 3.0	3.4 - 16	1.4 - 66
Uranium (ug/g)	0.6 - 9.9	5.5 - 256	0.06 - 520
Radium-226 (Bq/g)	0.01 - 0.09	0.2 - 0.8	0.01 - 34.1

* Based on stations apparently uninfluenced by the spill.

** Based on stations 1, 3, 4 and 6.

***From KLMC (1979).

TABLE 7: SUMMARY OF WATER QUALITY RESULTS FOR GERALD LAKE 1984-1985 |2|

PARAMETER	JANUARY 15 - JANUARY 17 1984 A	B	C	MAY 11 - MAY 13 1984 A	B	C	SEPTEMBER 25 - SEPTEMBER 28 1984 A	B	C	FEBRUARY 28 - MARCH 5 1985 A	B	C	MAY 21 1985 A	B	C	Sask. Surface Water Quality Objective
pH	7.1	8.7	8.9	7.7	7.7	7.6	7.4	7.4	7.4	6.6	6.5	6.6	6.7	6.8	6.8	6.5-8.5
Conductivity (ms/cm)	84	392	391	274	281	280	269	269	270	217	170	195	228	227	230	
Ca (mg/L)	5.6	58	67	46	47	46	45	49	46	45	56	52	39	40	39	
SO_4 (mg/L)	12	154	151	118	159	111	101	100	101	90	70	94	86	85	86	
NH_3 (mg/L)	0.3	6.8	2.5	2.7	2.8	2.8	1.0	1.0	1.0	0.4	0.4	0.4	0.1	0.1	0.1	
TSS (mg/L)	2.5	9.4	8.9	3.6	2.3	2.4	1.8	2.0	2.1	<1.8	<1.0	<1.3	1.5	2.0	2.5	
As (µg/L)	<5	12	11	6.6	6.3	6.5	<5	<5	<5	<5	<5	<5	<5	<5	<5	10
Pb (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05
Ni (mg/L)	<0.01	0.05	0.03	0.02	0.02	0.02	0.03	0.03	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.05
Ra-226 (Bq/L)	0.03	0.47	0.48	0.23	0.24	0.22	0.11	0.11	0.11	0.09	0.13	0.14	0.06	0.03	0.02	0.11
U (mg/L)	9.8	84	76	46	45	46	8.8	7.5	9.0	<5.5	<7.3	<6.3	<5.8	<5.0	<8.0	20

(1) Numbers presented are arithmetic means.

A = Surface
B = Mid-Depth
C = Bottom

TABLE 8: SUMMARY OF SEDIMENT CHEMISTRY RESULTS FOR GERALD LAKE 1984-1985 |2|

PARAMETER	JANUARY 15 - 17 1984	MAY 11 - 13 1984	MAY 21 1985
% Moisture	69	68	71
% LOI	40	24	27
SO_4 (μg/g)	5,200	5,328	5,800
Ca (μg/g)	2,520	3,554	3,431
P (μg/g)	4.00	415	535
TIC (%)	<0.10	0.10	<0.1
TOC (%)	19	12	13
TKN (μg/g)	110	7,466	7,858
Ni (μg/g)	18	66	67
Pb (μg/g)	<3.70	18	10
As (μg/g)	3.8	12	14
U (μg/g)	5.70	18	23
Ra-226 (Bq/g)	0.17	0.35	0.77
Pb-210 (Bq/g)	0.19	0.80	0.81
TL-230 (Bq/g)	0.05	0.77	0.28

(1) Numbers presented are arithmetic means.

TIC: Total Inorganic Carbon
TOC: Total Organic Carbon
TKN: Total Kjeldahl Nitrogen
LOI: Loss on Ingition

APPENDIX A

REPORT ON SPILL FROM WATER RESERVOIR NO. 2 |1|

January 5, 1984

A. Chronology:

Wednesday, Midnight

Supervisor observed that Water Storage Reservoir No. 2 was overflowing slightly, a trickle. Took immediate action to shut down mine water pumps and tailings pond supernatant pumps stopping all water flow into water storage reservoirs. Called service crew and initiated backfill to stop the overflow.

Thursday, January 5 - 2:00 a.m.

Efforts to stop the overflow were unsuccessful with overflow width at the top of the embankment about 6 to 7 metres wide, at this time. Haul trucks and dozers began placing material on the embankment to prevent it from collapsing.

Thursday, January 5 - 6:40 a.m.

A notch, approximately 1.5 metres deep, had formed and water from the reservoir continued to flow through this notch.

Thursday, January 5 - 8:10 a.m.

Senior management in the Saskatoon office were notified of the spill. At approximately 10:30 a.m., after making futher inquiries of the site, in order to gain a more accurate picture of the situation, Saskatchewan Environment and the Atomic Energy Control Board were notified of the spill.

Thursday, January 5 - 9:00 a.m.

Due to erosion of the sand behind it, the liner in Reservoir No. 2 had sagged and was down to a level approximately 4 metres below the original reservoir level. Water was flowing through the notch and began undercutting in the direction of the northwest corner of Reservoir No. 1 embankment.

During the next five hours, attempts to plug the notch with fill continued unsuccessfully.

Thursday, January 5 - 2:30 p.m.

At this time, the liner was cut at the notch to direct the water away from the foot of Reservoir No. 1 embankment preventing further undercutting.

Thursday, January 5 - 4:00 p.m.

The spill followed ground contours through the corner of the Gerald Lake muskeg area and was contained by the road leading to the Waste Management area. The rise in water was being monitored.

Thursday, January 5 - 4:30 p.m.

A representative from Saskatchewan Environment arrived on site. At this time, the notch was approximately 4 metres deep and 20 metres wide.

Thursday, January 5 - 5:30 p.m.

Escape of water from the muskeg area was prevented by the service road to the waste management facility. Water was beginning to encroach on this road and construction of a berm along the west side of the road commenced.

Thursday, January 5 - 7:30 p.m.

Flow from the reservoir had diminished to an estimated 900 litres per minute.

Thursday, January 5 - 8:30 p.m.

Flow from the reservoir continued to diminish and was estimated at approximately 700 litres per minute. The two culverts under the service road which connect the muskeg area to a trench leading to Wolf Lake were re-examined to confirm that no water was escaping through the frozen culverts.

Thursday, January 5 - 10:30 p.m.

Flow from the reservoir had slowed to an estimated 500 litres per minute. The water samples that had been collected earlier were flown to Saskatoon for analyses by the Saskatchewan Research Council. Work on the containment berm along the service road continued through the night.

Friday, January 6 - 7:00 a.m.

Feedlines to the reservoirs were rechecked to confirm that no more water was entering the reservoirs. Flow now estimated at approximately 200 litres per minute from Reservoir No. 2.

During the day, work on the berm along the service road continued to ensure that the berm was of sufficient height to contain the ice pressure.

Friday, January 6 - 3:00 p.m.

Repairs to the lamella thickener in the mill were completed and the mill began to withdraw water from Reservoir No. 2.

Friday, January 6 - 5:00 p.m.

Flow from the reservoir had slowed to a trickle.

Friday, January 6 - 10:30 p.m.

Flow from Reservoir No. 1 into Reservoir No. 2 had ceased although a trickle of water still was flowing out of Reservoir No. 2.

A temporary berm along the east side of the service road, adjacent to the reservoirs, was built to contain any further leakage.

Saturday, January 7 - 6:40 a.m.

Flow from Reservoir No. 2 stopped.

Saturday, January 7 - 3:15 p.m.

A meeting was held among representatives of Key Lake Mining Corporation, Saskatchewan Environment and their respective consultants. The meeting was held to discuss alternatives for remedial work of the damaged portion of the reservoir embankment, treatment of the spilled contaminated water and corrective measures to prevent similar occurrences.

GROUND WATER CLEANUP ACTION

VERONA WELL FIELD

BATTLE CREEK, MICHIGAN

By

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Prepared For

Technical Seminar on Chemical Spills
Montreal, Quebec
February 5-7, 1986

* Address: Fruehauf Corporation
R&D Division
Detroit, Michigan

ABSTRACT

Volatile organic compounds (VOC's) were identified in the municipal water supply in the City of Battle Creek, Michigan. Ground water investigations revealed that the VOC's had contaminated 27 out of 30 municipal wells in the Verona Well Field, and that the City's entire water supply was threatened. A hydrodynamic, ground water, purge system was designed and installed to limit the contaminant migration. The purge system created an artificial barrier that restricted and actually reversed the contaminant migration. This report focuses on: 1) The installation of the purge/treatement system; 2) problems during construction; 3) system operation; and 4) the effects the purge system has had on controlling the spread of contamination.

1.0 SUMMARY OF EVENTS

1.1 Site Location

The Verona Well Field is located on the northeast edge of the City of Battle Creek, in the eastern one half of section 32, T15, R7W of Calhoun County, Michigan (see Figure 1). The well field incorporates property on both sides of the Battle Creek River. The area north and east of the well field is essentially rural. Land use south and west is light to heavy industrial. A residential area is located directly south, and the Grand Trunk and Western Railroad (GTWRR) marshalling yard borders the well field's eastern edge.

1.2 Site Description

The well field consists of three wells west of the Battle Creek River (in Bailey Park), along with 27 wells, and the major pumping/water treatment station, east of the river (Figure 2). All wells yield between 300 and 1000 gpm (gallons per minute). The principal aquifer for the well field is the Marshall sandstone formation. Water transmission through the Marshall formation occurs primarily through fractures in the sandstone.

The Verona Well Field provides potable water to the City's 35,000 residents, and part, or all of the water used by three major food processing companies and various other commerical and industrial establishments. A review of the monthly pumpage rates for the past two years indicates that the City requires an average water supply of approximately 10 MGD (million gallons per day), with additional supplies as high as 19 MGD necessary to meet peak demand periods during the summer months.

1.3 Initial Situation

In August 1981, the Calhoun County Health Department's (CCHD) routine testing of private wells revealed that the water supply from Verona Well Field was slightly contaminated with volatile hydrocarbons. Testing by the CCHD and the Michigan Department of Public Health (MDPH) indicated that 10 City wells were contaminated with detectable levels of volatile chemicals. The MDPH initiated weekly sampling of the well field, and also began sampling residential wells south of the well field. Their results showed that approximately 80 private wells in the area contained the contaminants. Several residential wells had total volatile organic compound (VOC) contamination levels near 1,000 ug/l (micrograms per liter, or parts per billion). One well had a dichloroethylene concentration of 3,900 ug/l.

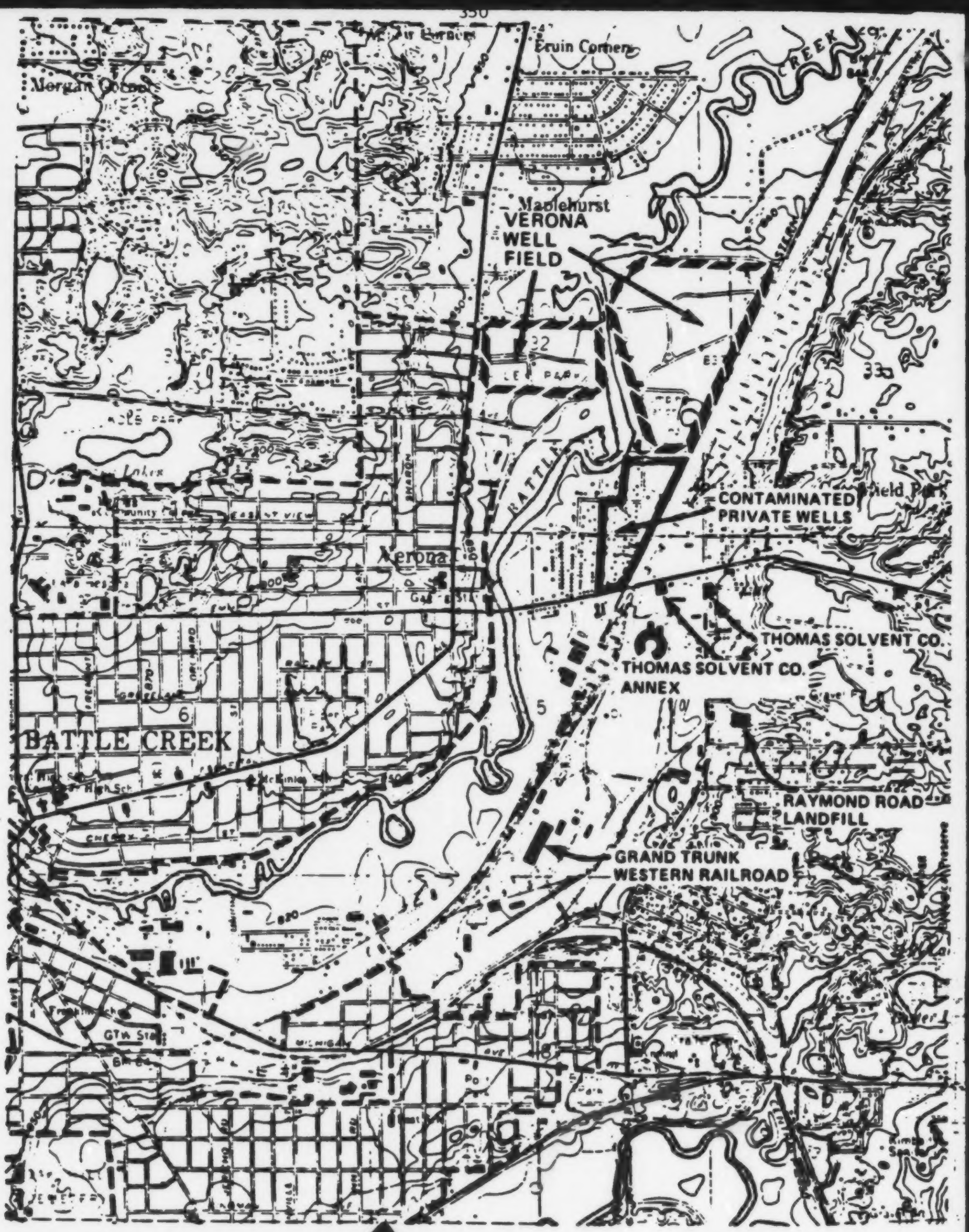
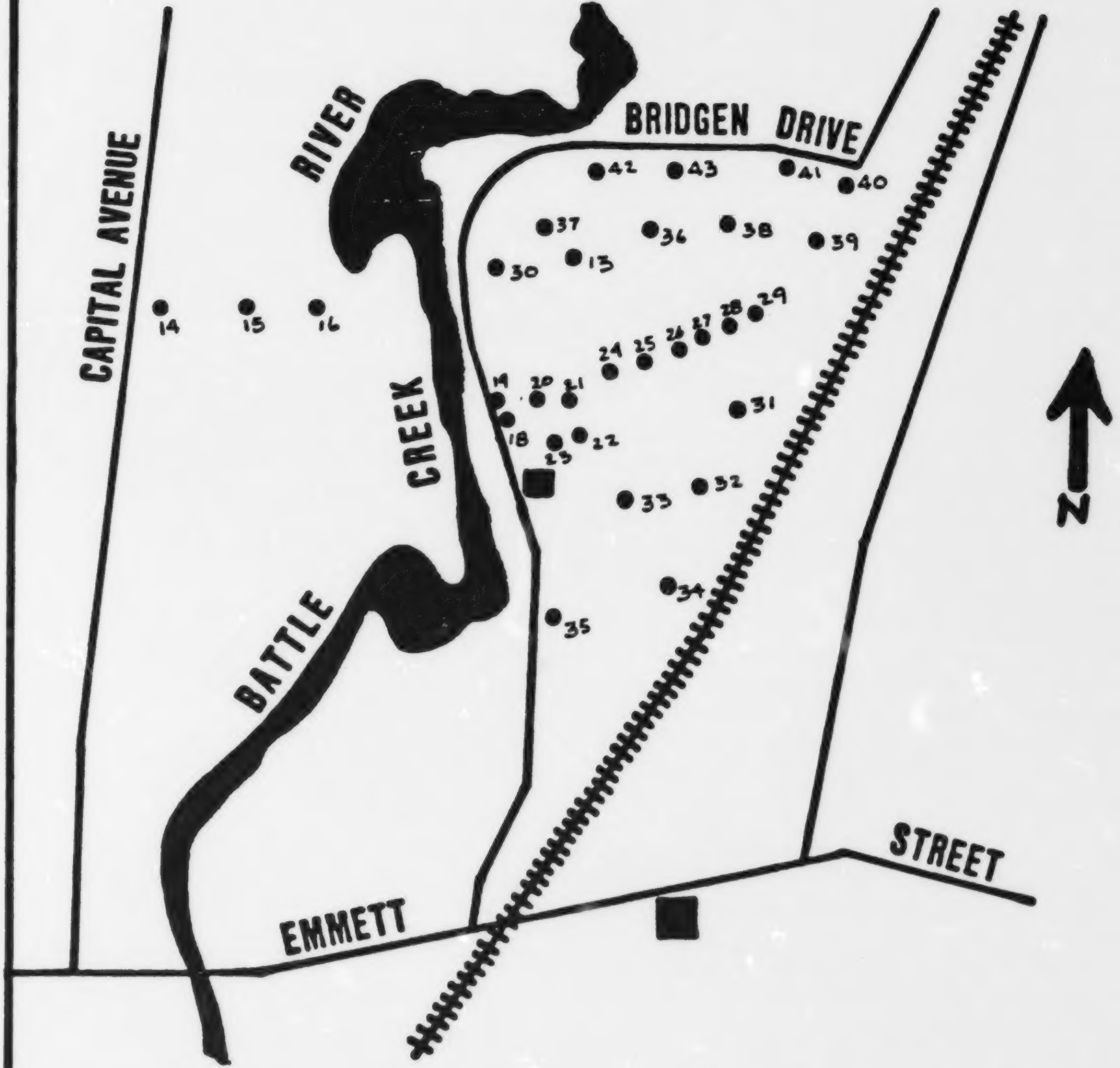

350
Morgan Corner
Bruin Corners
CREEK
Maplehurst
VERONA
WELL
FIELD
32
33
BATTLE
Lakes
CONTAMINATED
PRIVATE WELLS
Field Park
Verona
THOMAS SOLVENT CO.
THOMAS SOLVENT CO.
ANNEX
5
6
BATTLE CREEK
RAYMOND ROAD
LANDFILL
GRAND TRUNK
WESTERN RAILROAD
CITY LIMITS
N

Figure 1
SITE LOCATION
VERONA WELL FIELD

VERONA WELL FIELD


CAPITAL AVENUE
RIVER
BRIDGEN DRIVE
BATTLE
CREEK
EMMETT
STREET
N
42
43
41
40
37
36
38
39
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33
32
34
35

Figure 2

Several studies were conducted to delineate the contaminated areas: These include:

- The Michigan Department of Natural Resources (MDNR) industrial survey to determine potential contamination sources. This survey identified the Thomas Solvent Company (TSC) facilities, the GTWRR, and the Raymond Road Landfill as possible contaminant sources.

- The U.S. Environmental Protection Agency (U.S. EPA) Technical Assistance Team (TAT) Spring 1982 ground water survey. The results showed that a ground water divide exists in the upper aquifer near Emmett Street. The TAT study further concluded that the source of contamination was in the vicinity of the TSC properties (Figure 1).

- The U.S Geological Survey (USGS) hydrological investigation under a contract with the City of Battle Creek. The study examined the area's geology and ground water flow patterns. The USGS also prepared a flow model that evaluated the effects of well field pumping on ground water flow.

In July of 1982, the Verona Well Field was placed on the National Priorities List (Group 4), and became eligible for a Federal cleanup ulitizing CERCLA money. At this time, the U.S. EPA also implemented a bottled water program for affected area residents. A new water distribution system was constructed to provide City water to the affected area. When the system was completed in early January 1984, the bottled water program was discontinued.

The U.S. EPA began its Remedial Investigation (RI) in November 1983. The first phase, completed in Spring 1984, defined the exact nature and extent of both the horizontal and vertical contamination. This phase involved installing ground water monitoring wells and collecting water and soil samples throughout the area. The second phase pinpointed the exact sources of the contamination and further defined the physical characteristics of the aquifer itself.

In February 1984, the TSC was ordered by the U.S. EPA to purge the immiscible layer of contaminants from the ground water beneath the Company's main facility. This layer of solvents was identified during the first phase of the RI. The TSC, a formulator of solvents, undertook the action, purged 500 gallons of contaminated ground water, and continued to monitor the ground water until early 1985.

In January 1984, the Michigan Attorney General filed a civil complaint for injunctive relief against the TSC. The complaint sought remediation of soil and ground water contamination at both TSC facilities upgradient from the Verona Well Field. In March 1984, an order was entered in favor of the state. The TSC responded to the order by filing a petition for bankruptcy under Chapter 11 of the State's Bankruptcy Code.

It is important to note that during Phase I of the RI, the two TSC facilities located approximately 1/2 mile upgradient of the well field were found to contain high levels of soil and ground water contamination. Analyses of water taken from monitoring wells located at each facility showed the following levels of contaminants:

1,1,1 Trichlorethane	up to 3,500 mg/1
Trichlorethylene	up to 44,000 mg/1
Perchlorethylene	up to 56,000 mg/1
1,2 Dichloroethane	up to 2,200 mg/1

The concentration and migration of contaminants into the well field (Figures 3 and 4), indicated a deteriorating situation. Figure 3 shows the plume as it existed in early 1982. Figure 4 illustrates the results of sampling at the end of 1983. The contaminated ground water plume was clearly moving northward, and threating to encompass the entire well field.

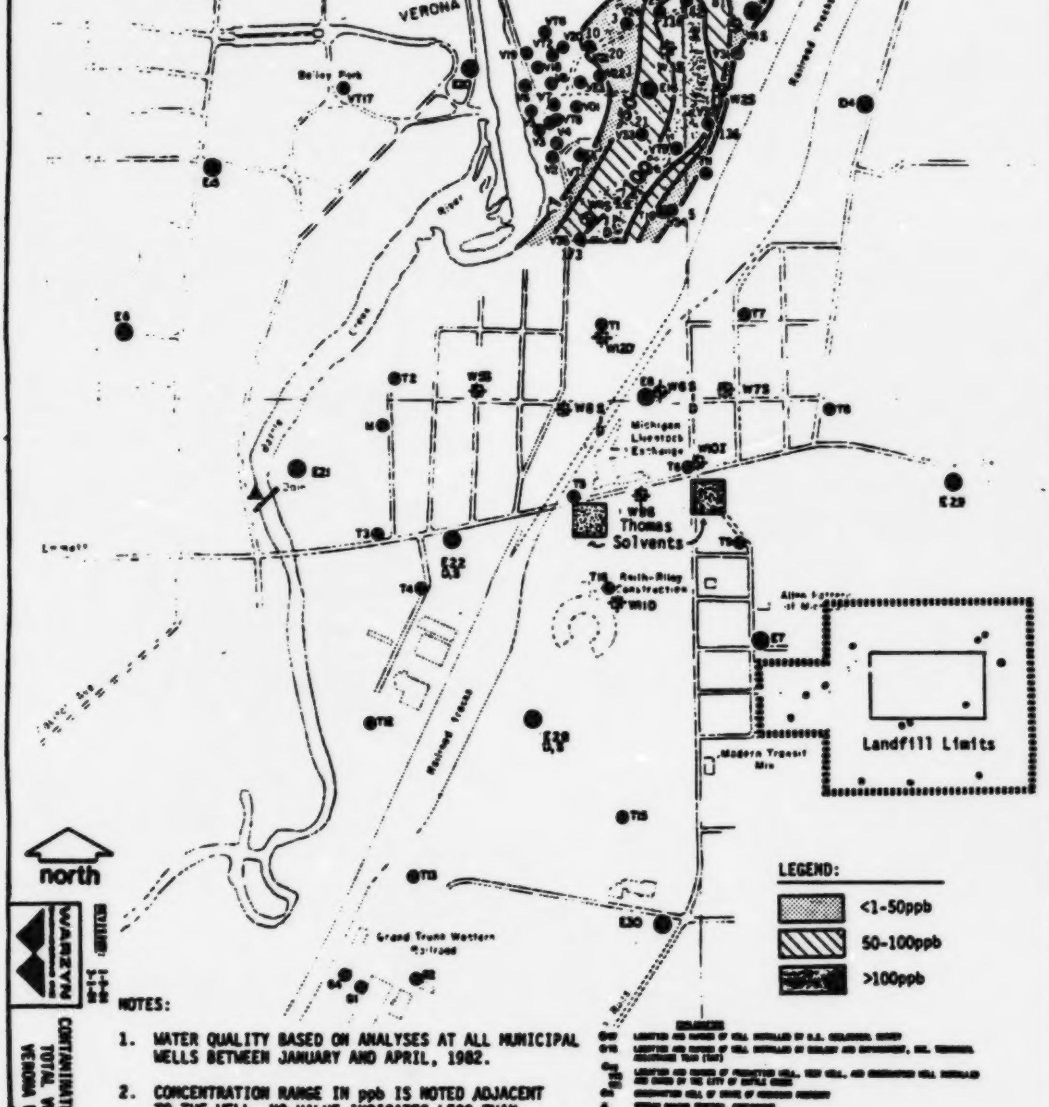
The continued deterioration of the well field posed an unacceptable threat to human health. Therefore, a Focused Feasibility Study (FFS) was prepared to examine removal options which would protect human health and minimize the further spread of contamination. The FFS recommended the installation of a ground water purge/barrier system. This temporary solution would purge contaminated water by pumping five existing site wells to create a ground water barrier which would prevent further northward migration of contaminants. The water purged from the wells would be treated by an air stripper to remove the contamination, and then it would be discharded to the Battle Creek River.

The air stripper construction and fabrication was estimated to take six months. Based on this estimate, by the time the air stripper was operational, it would no longer be effective. The FFS had predicted that if the purge/barrier system was not operating by late May, the contaminant plume would continue to migrate northward into the well field, but the migration rate would be greater due to the increased summer water demand. Therefore, the longer the implementation of the purge system was delayed, the greater the probability that the spread of contamination could not be controlled or reversed. It was conceivable that the entire well field and city water supply would become highly contaminated. As a result, it was decided to use a temporary, granular activated carbon (GAC) system to treat the purged water until the air stripper could be installed.

1.4 Federal Cleanup Actions

On March 20, 1984 the U.S. EPA initiated efforts to install the purge/barrier system (FFS March 1984), and avert a potential potable water shortage in Battle Creek, Michigan. An air stripper had been chosen to remove the VOC's from the purged water before its discharge to the river. Construction estimates showed that the system would not be operational until late July. Plume migration trends indicated that this would be too late to effectively mitigate the spread of contamination. It was recommended that a temporary GAC system be installed and operated until the air stripper could be fabricated and constructed.

Due to the previous Immediate Action at this site (1983 bottled water program; see Section 1.3), it was necessary for the Region to obtain both an exemption from the six month limit on Immediate Actions, and authorization for expenditure of additional funds.

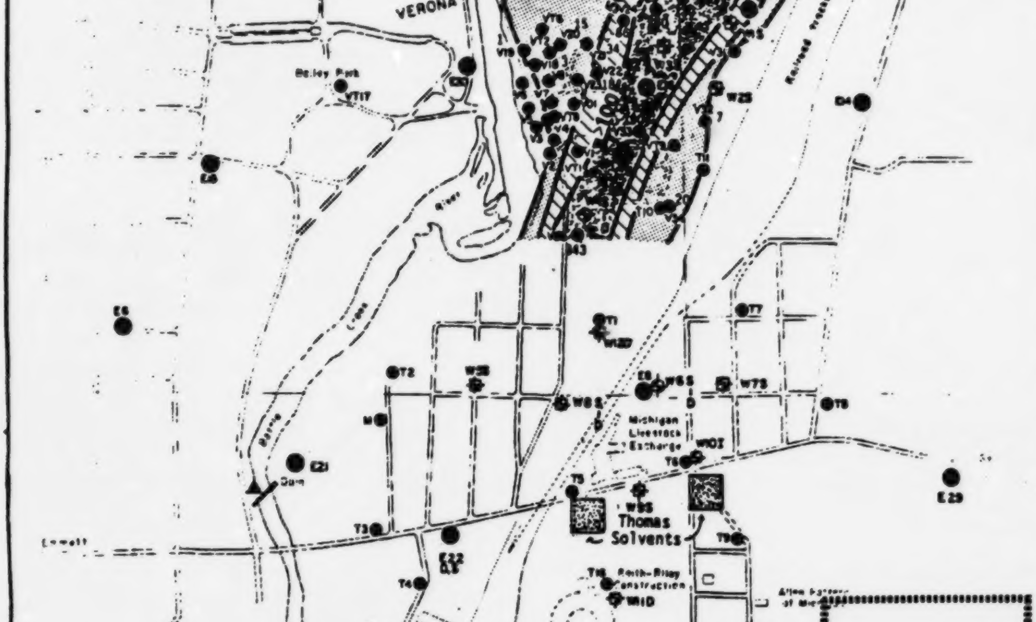

north
WARZYN
VERONA
WELL
Bailey Park
Bridgeton Dr
Railroad tracks
Michigan Livestock Exchange
Thomas Solvents
Raith-Riley Construction
Landfill Limits
Modern Transit Mix
Grand Trunk Western Railroad
Emmett
Dam
LEGEND:
<1-50ppb
50-100ppb
>100ppb
0
.25
.5 MILES
0
.25
.5
.75 KILOMETERS

CONTAMINATED WELL FIELD AREA
TOTAL VOC 1/82 - 4/82
VERONA WELL FIELD-FFS

NOTES:

1. WATER QUALITY BASED ON ANALYSES AT ALL MUNICIPAL WELLS BETWEEN JANUARY AND APRIL, 1982.
2. CONCENTRATION RANGE IN ppb IS NOTED ADJACENT TO THE WELL. NO VALUE INDICATES LESS THAN DETECTION (1 ppb).
3. WATER QUALITY ANALYSES WERE OBTAINED FROM THE CITY OF BATTLE CREEK.
4. BASE MAP ADAPTED FROM USGS PLANIMETRIC MAP.

FIGURE 3


E2
E35 0.5
VT3
353
E27
E3
E32
E33
E10
Bridges Dr
E4
VERONA
WELL
50
100
Bailey Park
V15
V16
V17
E5
VT17
E31
E6
E9
W25
River
Railroad Tracks
Battle Creek
T1
T7
T2
W28
W8S
E8
W6S
W7S
T8
M
Michigan Livestock Exchange
W0I
T6
T5
E21
Dam
W5S
Thomas Solvents
T9
T3
Emmett
E22 0.5
T4
T11
Roth-Riley Construction
W1D
Allen Systems of Mich.
E7
T12
E28 0.5
Railroad Tracks
Landfill Limits
Modern Transit Mix
T16
T13
E30
E29
north
Grand Trunk Western Railroad
Kellogg Co.
WARZYN
LEGEND:
>1-50ppb
50-100ppb
>100ppb
0
.25
.5 MILES
0
.25
.5
.75 KILOMETERS

CONTAMINATED WELL FIELD AREA
TOTAL VOC 9/83 - 1/84
VERONA WELL FIELD-FFS

NOTES:

1. WATER QUALITY BASED ON ANALYSES AT ALL MUNICIPAL WELLS BETWEEN JANUARY AND APRIL, 1982.
2. CONCENTRATION RANGE IN ppb IS NOTED ADJACENT TO THE WELL. NO VALUE INDICATES LESS THAN DETECTION (1 ppb).
3. WATER QUALITY ANALYSES WERE OBTAINED FROM THE CITY OF BATTLE CREEK.
4. BASE MAP ADAPTED FROM USGS PLANIMETRIC MAP.

FIGURE 4

The extension and the extramural funding were approved April 20, 1984 at which time the Deputy Project Officer for the Emergency Response Cleanup Services (ERCS) contract issued delivery order number 6894-05-008 (DO) to the ERCS contractor.

The DO called for an on-site meeting between the U.S. EPA Project Manager/On-scene Coordinator (OSC) and the ERCS Response Manager on Wednesday April 23, to discuss the project and to begin making the necessary arrangements for supplies and contractors. During that meeting, it was discovered that the Verona Well Field distribution lines were gravity flow. Therefore, a lift station would have to be constructed to provide the hydraulic head necessary to run the temporary carbon filtration units.

Site work began on Friday, April 27, when response personnel spent the day working to locate and excavate various underground structures in the well field. Site work resumed on Thursday, May 3, when the contractor began digging the trench for the by-pass line which would isolate the purge wells from the municipal supply wells. At that time, a MDPH represenative informed the OSC that isolation of the purge wells could not be completed until the 30 series wells bypass, previously installed by the City, was removed. (The 30 series refers to wells 31 through 35.) The MDPH stated that unless this action was taken, the City would not have an adequate potable water supply available during peak demand periods. The OSC directed that the bypass be located and removed. This task was not completed until Friday afternoon May 4.

On Wednesday May 9, installation of the 20 series bypass header line was completed (See Figure 5). Two carbon treatment units were delivered to the site and readied for use that day, and by Friday, May 11, all four vessels had been set in place, assembled, and filled. Response personnel began working to fabricate and install the piping for the lift station. This proved to be the critical time consuming phase of the construction, therefore, additional welders and pipe fitters were brought in and overtime was authorized by the OSC.

Slumping of the sides was a re-occurring problem during the lift station excavation. To minimize this problem, the size of the excavation was increased, and the sides were sloped. Framing of the floor and footings began on Friday May 11, and was completed by Tuesday, May 15, at which time thirty-three yards of concrete were poured to form the lift station foundation.

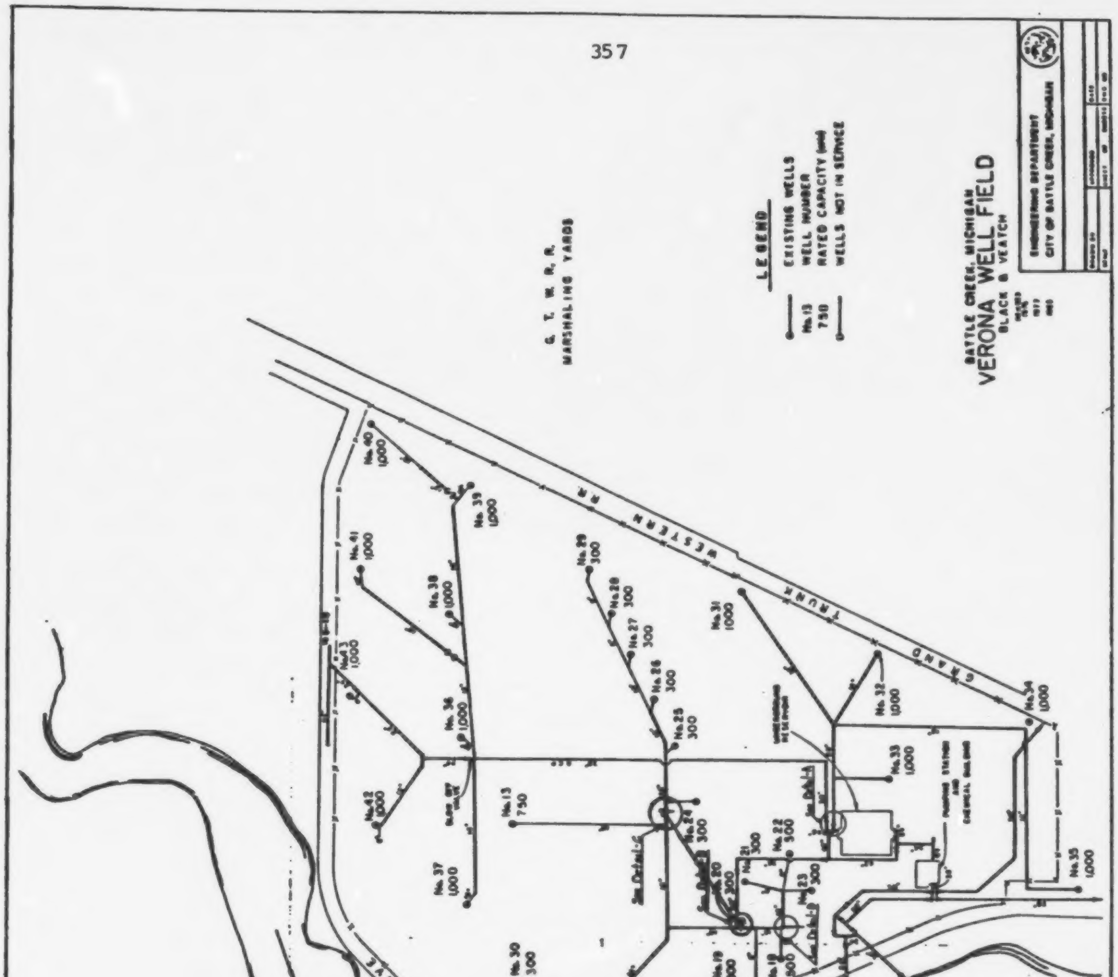

BATTLE CREEK, MICHIGAN
VERONA WELL FIELD
BLACK & VEATCH
LEGEND
EXISTING WELLS
WELL NUMBER
RATED CAPACITY (gpm)
WELLS NOT IN SERVICE
No.13
750
G. T. W. R. R. MARSHALING YARDS
GRAND TRUNK WESTERN RR
BRIGDEN DRIVE
BATTLE CREEK RIVER
BAILEY PARK
CAPITAL AVENUE N.E. (M-78)
No.14 750
No.15 750
No.16 750
No.17 750
No.18 500
No.19 300
No.20 200
No.21 300
No.22 300
No.23 300
No.24 300
No.25 300
No.26 300
No.27 300
No.28 300
No.29 300
No.30 300
No.31 1000
No.32 1000
No.33 1000
No.34 1000
No.35 1000
No.36 1000
No.37 1000
No.38 1000
No.39 1000
No.40 1000
No.41 1000
No.42 1000
No.43 1000
PUMPING STATION AND CHEMICAL BUILDING
SCALE IN FEET
ENGINEERING DEPARTMENT
CITY OF BATTLE CREEK, MICHIGAN

Figure 5

Form work for the lift station's 12-foot high walls began on Wednesday, May 16. Two days later, fifty-three yards of concrete were poured in three, separate, four-foot high sections utilizing a 50-ton crane and a concrete bucket. The outside walls were then sealed and the area surrounding the lift station was backfilled. An emergency wet well overflow line was installed and connected to the old pump station's discharge line to the Battle Creek River. This line had been previously located, excavated, and cleaned.

Pipe was cut and welded from the 11th to the 20th of May. Final assembly of the sections began on May 20, and pipe installation was completed four days later.

Throughout the entire construction process, electricians were on site installing equipment. By Thursday, May 24, most controls and alarms had been installed, but due to shipping problems, the actual water level probes had not yet been delivered.

On Friday afternoon, May 25, after the pumps had been balanced and aligned, and the well field lines had been flushed clean, the purge system was activated. Due to the lack of automatic controls, the system was operated manually until Tuesday, May 29, when the probes were installed.

By Wednesday, May 30, the carbon units began to experience problems with rapid pressure build up (see Section 3.1 for details). On Tuesday, June 12, a fifth carbon vessel was delivered to the site, connected to the system, and put in operation the following day. Late that week, all piping inside the dry well was insulated to prevent the excessive condensation and dripping.

Weekly analytical testing was performed to ensure that none of the five carbon vessels reached the break through point. Regular backwashing of the carbon units was performed to keep the system operating and to ease pressure build ups. The purge/barrier system operated smoothly until early September, when the backwashing had to be performed daily to relieve the pressure build ups. On September 19, the carbon filters were replaced with the newly constructed air stripper. The carbon vessels remained on site, for an additional month, and were used as a back-up system for the air stripper during its debugging period.

During the week of October 22, the five carbon vessels were emptied and shipped back to the vendor. All piping which serviced the carbon filters was dismantled. Efforts were made to sell this material as used pipe, but to no avail. The material was subsequently sold as scrap. Finally, the site was cleaned and graded to the levels of the surrounding topography.

1.5 State Efforts to Cleanup the Site

Efforts undertaken by the MDNR and the MDPH during the Verona Well Field investigation were extensive. The MDPH routinely collected and analyzed residential and municipal drinking water samples and monitored municipal well rotations to keep contaminated water levels to a minimum. The MDPH data was incorporated into the U.S. EPA hydrogeologic studies to identify the contaminated plume's migration. The MPDH also advised area residential well users to seek an alternative drinking water supply, such as the municipal supply or bottled water.

The MDNR coordinated information from local citizens and industrial users and compiled a list of potential contaminant sources. The MDNR also conducted an industrial survey to determine solvent usage in the area. On March 7, 1984, the MDNR was successful in obtaining a preliminary injunction against the TSC to abate a public nuisance. The preliminary injunction required that the TSC test all storage tanks for leakage, remove materials identified on the Michigan Critical Material List from the site, remove contaminated material from monitoring wells, and propose a feasible cleanup plan for the site.

On May 4, 1984, a joint preliminary injunction was issued against the TSC and the GTWRR. This injunction required the TSC to remove the contamination from below its facility by purging the ground water and treating the contaminants with granular activated carbon. To date, this injunction has not been enforced because the TSC has filed for bankruptcy.

1.6 Local Government Agency Efforts During the Cleanup

The Verona Well Field is situated on City owned property, and various City departments cooperated in the cleanup action. The Public Utilities Director provided the communication link between City departments. He also provided site security and survelliance by increasing police patrols in the area. The City furnished a back hoe, trash pump, vactor truck, fire hose, and a number of other items during this project. The Verona pumping station provided office space, telephones, a refrigerator, and use of their basic water quality laboratory. A maintenance engineer at the pumping station was hired by the ERCS contractor to regularly service the carbon treatment system. After the carbon units began experiencing the high pressure build ups, the CCHD offered to have their laboratory perform bacteriological testing to determine if iron reducing bacteria were present. The CCHD graciously provided these analyses to this project at no charge.

1.7 Summary of Expenditures

The following is a breakdown of costs incurred under the ERCS contract for this Immediate Action.

Immediate Action #1 (Bottled water)	$28,000.00
Immediate Action #2 (Purge/barrier system)[1]	
1.) ERCS Contractor	
- Labor	$22,897.30
- Travel & Subsistence	5,479.38
- Mileage	358.40
- Equipment	357.00
- Materials	6.08
- Transportation	0.00
- Sampling/Analytical	17,080.00
	$46,178.16
2.) ERCS Subcontractors	
- Carbon Vendor	
a) Accelerated Carbon Test	4,160.00
b) Activated Carbon	107,500.00
c) Carbon Filter Vessels	85,775.00
d) Removal of Spent Carbon	12,000.00
	$209,435.00
- Central Iron and Metal Company	-181.75
- Clark Construction Company	312.00
- Consumers Power Company	369.60
- Drake Insulations, Inc.	2,223.02
- Jack Saye	10,922.00
- William H. Kelly Company	1,800.00
	$224,879.87
3.) Modification/Demobilization	0.00
4.) Fixed Rate Labor	$71,866.75
5.) Fixed Rate Equipment	$28,012.50
6.) Reimbursable Materials	
- Alro Steel Corporation	186.42
- Aurora Pump (Faber Pump & Equipment)	7,217.60
- Clark Oil	28.85
- Corlett Lumber Company	636.37
- F&A Fabricating, Inc.	748.00
- F.D. Lawrence Electric Company	4,091.40
- Galloup Pipe & Supply Company	26,923.66
- G.W. Northrop, Inc.	100.00
- Hausman Steel Corporation	1,314.56
- Hoffman Brothers, Inc.	2,118.15
- Hunter - Prell Company	3,447.64
- J.H. Ballenger Company	333.71
- Kalamazoo Fabricating	294.30
- Kendall Electric, Inc.	2,119.66
- Kendall Industrial Supplies, Inc.	234.85

- Modern Transit Mix	4,556.81
- Murray Construction Company	650.25
- Neenah Foundry Company	462.91
- Northern Concrete Pipe, Inc.	1,788.29
- Ryerson Steel	1,064.29
- Summit Industries, Inc.	3,097.38
- Underground Pipe & Valve, Inc.	19,900.82
- Union Electric, Inc.	4,423.17
- Van Tran Electric Corporation	4,986.00
	$90,725.07

7.) Reimbursable Transportation/Shipping

- Airborne	23.00
- Air Couriers International	2,906.25
- Air Wisconsin, Inc.	9.68
- Emery Worldwide	152.14
	$3,091.07

8.) ERCS Handling Charge (3%)

- Materials	2,721.93
- Transportation	92.73
- Subcontracts	948.15
	3,762.81
Total ECRS Cost:	$468,516.23

U.S. EPA Costs

- Labor	9,785.98
- Travel	6,521.69
	16,307.67
TAT Costs	22,028.32
Total Project Cost[2]	$506,852.22

Notes: 1. This delivery order is currently undergoing an audit by the U.S. Inspector General's Office, and will not be definitized until that audit is completed. Therefore, until the audit and definitization are completed, these numbers can not be considered as final costs.

2. This is not a final cost. It will not be finalized until after the contract modification, audit, and project definitization are completed.

1.8 Community Relations

An effective community relations program is an important aspect of CERCLA activities. The sensitive and emotional nature of hazardous waste sites in a community requires that much time be spent on the community relations. An underestimation can result in serious consequences. In the past, local residents were frustrated by what they perceived to be unnecessary delays, broken promises, and a general cover-up on the part of the government agencies involved. The citizens had had problems obtaining informaton and contacting officials with their fears. These problems had been alleviated, but there was still a sense of mistrust of government officials among the residents.

Due to the past problems, the community relations program for this project was designed to be a very open one. The well field is situated adjacent to a residential area, so there was frequent contact with the residents. The citizens were encouraged to visit the site and ask any questions they may have had. The OSC was available daily at the site to answer questions, and to explain how the purge system would affect the community. During the course of the project, numerous residents visited the site and observed the construction process. The local newspaper and television stations kept the citizens well informed of the project's progress.

1.9 Public Health

The contaminants found in the Verona Well Field are primarily volatile chlorinated hydrocarbons. Five of the compounds are suspected carcinogens (1,2 dichloroethane; 1,1,1 trichloroethane; 1,1 dichloroethylene; trichloroethylene; and perchlorethylene). The contaminant characteristics of all the compounds detected are summarized in Table 1. Prior to this action, the City had been able to provide an acceptable quality water supply, by blending contaminated and uncontaminated water. However, as the plume continued to migrate into the well field, the contaminant levels in the wells continued to increase. During the upcoming summer months, the increased demand would only stress the aquifer resulting in an accelerated deterioration of the well field. This posed a significant risk to human health because blending would soon cease being an effective method for minimizing the public's exposure to the contamination.

Table 1
CONTAMINANT CHARACTERISTICS

DRAFT

Contaminant	Highest Observed Concentration (µg/1)	Long-Term Health Advisory (µg/1)	Cancer Risk Level	
			10^{-5} (µg/1)	10^{-6} (µg/1)
Frequently Detected				
1,1 Dichloroethane (1,1 DCA)	34	-	-	-
1,2 Dichloroethane (1,2 DCA)	8	-	6.0	0.6
1,1,1 Trichloroethane (1,1,1 TCA)	150	1,000	220	22
cis-1,2 Dichloroethylene (cis 1,2 DCE)	229	-	-	-
1,1 Dichloroethylene (1,1 DCE)	11	-	0.34	0.034
Trichloroethylene (TCE)	62	75	28.0	2.8
Perchlorethylene (PCE)	94	20	9.0	0.9
Sporadically Detected				
Methylene Chloride*	5.6	150	1.9	0.19
1,2 Dibromoethane*	3	-	0.55	0.055**
Chloroform*	15	-	1.9	0.19
Benzene*	9	70	6.7	0.67
Ethylbenzene*	5	-	-	-
Toluene*	57	100**	-	-
Xylene*	26	-	-	-
1,2 Dichlorobutane*	detected	-	-	-
Vinyl Chloride*	1	-	10.0	1.0**
trans-1,2-dichloroethylene*	detected	-	-	-

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* Sporadic, generally nonrecurring contaminants observed in some Verona wells.

** These levels were established by the National Academy of Sciences. All others were taken from the USEPA and the Cancer Assessment Group.

After the ground water purge/barrier system was installed, effluent samples of the discharge were collected on a weekly basis. Criteria for the water discharged to the river was established by the U.S. EPA based on the MDNR recommendations. The effluent criteria for total VOC's was never exceeded during the Immediate Action.

Due to the potential for volatilization of the organic contaminants, air sampling was periodically conducted. No readings above background levels were ever obtained in any of these samplings.

2.0 EFFECTIVENESS OF REMOVAL ACTIONS

2.1 Responsible Parties

Two potentially responsible parties (PRP's), the TSC and the GTWRR, have been identified to date. Both PRP's declined to conduct the RI/FS in April 1983, and both declined, in late April 1984, to undertake the installation of the purge/barrier system.

In February 1984, TSC was ordered by the U.S. EPA (unilaterial Section 106 Administrative Order) to purge an immiscible layer of contaminants from the ground water beneath the Company's main facility. The TSC voluntarily undertook that action and continued to regularly monitor the remaining contaminants until Spring of 1985 when their consultant ceased the regular checks due to the bankruptcy actions by the TSC.

2.2 State And Local Agencies

The MDNR had limited involvement during this Immediate Action. The U.S. EPA directed and funded all activities. The MDNR also provided the criteria which was used to establish the effluent discharge limits to the Battle Creek River. MDPH officials sampled the City's wells weekly and provided analytical results which were used to evaluate the purge/barrier system effectiveness. Both agencies also regularly provided their comments and suggestions on the project to the U.S. EPA.

CCHD Officials were extremely cooperative. They provided both bacteriological and basic water quality analysis on the influent and backwash waters. These analytical results were helpful in determining the potential cause of the pressure build up on the carbon vessels.

Various Battle Creek City departments were instrumental during this action. The Public Utilities Director, provided the communication link with the City's departments. The water department provided a trash pump which was used during dewatering of the lift station excavation, and they supplied a vactor truck to clean the excavated water and sewer lines. The City provided office space and a telephone for the U.S. EPA, TAT, and ERCS in the Verona Pump Station. Operators at the station, provided knowledge and technical expertise on pump systems and were also instrumental in identifying the well field header system locations.

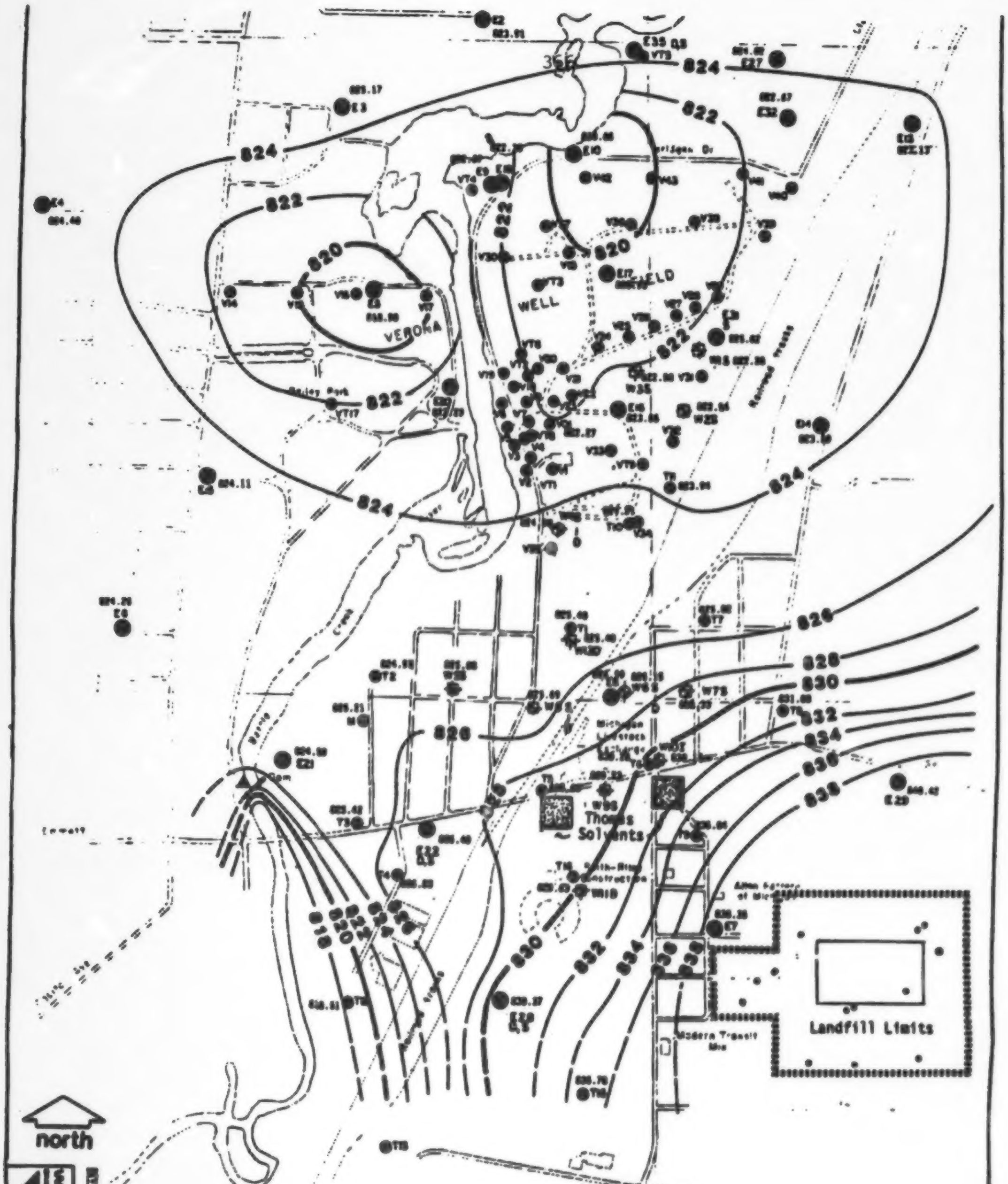
2.3 Federal Agencies

The objective of this Immediate Action was to prevent the further enroachment of contaminants into the remaining "clean" wells at the north end of the well field. The objective was accomplished by installing a purge/barrier system. The system was designed by hydrologists and geologists at the USGS and created a hydraulic ground water divide which prevented further northward migration of the contaminant plume. Municipal wells V20, V22, V25, V27 and V29 were selected as the purge wells. A small pump, or lift, station was constructed to pressurize the water prior to filtration and discharge to the river. A granular activated carbon filtration system was used to treat the purged water. The purge system's effectiveness was measured by the changes in the water quailty of the northern production wells (V13, V30, and V36 through V43) and by the presence of a distinct cone of depression around the purge wells. This distinct cone effectively prevents contaminant migration north of the purge system. Figures 6 and 7 show the water table as it existed both before (February 1, 1984) and after (August 11, 1984) the purge system was activated May 25, 1984. Figure 8 illustrates the change through time of total VOC's at three wells north of the purge system, wells V13, V38, and V39. This graph shows that prior to the May 25, start-up date of the purge/barrier system, contaminant concentrations in the northern wells were steadily increasing. After the system was actuated, a noticeable downward shift occured in each well. The carbon filtration system was replaced with an air stripper, on September 19. By that date, the total VOC's in the ten production wells north of the purge line had dropped from a high of 130 ppb on May 22, to only 2 ppb. Since September 1984, eight of the ten wells north of the purge system have remained completely free of contaminants, and two of the ten have sporadically shown only 1 ppb of total VOC contamination.

3.0 PROBLEMS ENCOUNTERED AND RECOMMENDATIONS

3.1 CARBON UNIT PROBLEMS

There were various problems associated with the carbon units. When the system was put into operation pressure drops across the units would rise to extremely high levels in very short periods of time. Vendor representatives suggested that the problem could be caused by a number of things, one of which was that the four vessels could not handle the flow. To correct this a fifth vessel was installed, and the system's potential capacity was increased from 1800 to 2250 gpm. However, this did not solve the problem. Vendor representatives, CCHD officials, pump station operators, TAT representatives, and ERCS engineers offered a variety of causes and possible solutions to the problem. These included clogging


824
822
820
VERONA
WELL
FIELD
826
828
830
832
834
836
838
818
Thomas Solvents
Landfill Limits
north
WARZYN
0
.25
.5 MILES
0
.25
.5
.75 KILOMETERS

NOTES:

1. WATER LEVELS OBTAINED FROM USGS.
2. RIVER STAGE AT THE DAM IS APPROXIMATELY 823.7 ABOVE DAM AND 818 BELOW DAM.
3. WATER LEVELS AVAILABLE ARE NOTED ADJACENT TO WELL.
4. WATER TABLE CONTOURS ARE DASHED WHERE INFERRED.
5. WELL LOCATIONS ARE APPROXIMATE.
6. BASE MAP ADAPTED FROM USGS PLANIMETRIC MAP.

WATER TABLE MAP
FEBRUARY 1, 1984
VERONA WELL FIELD-FFS

FIGURE 6

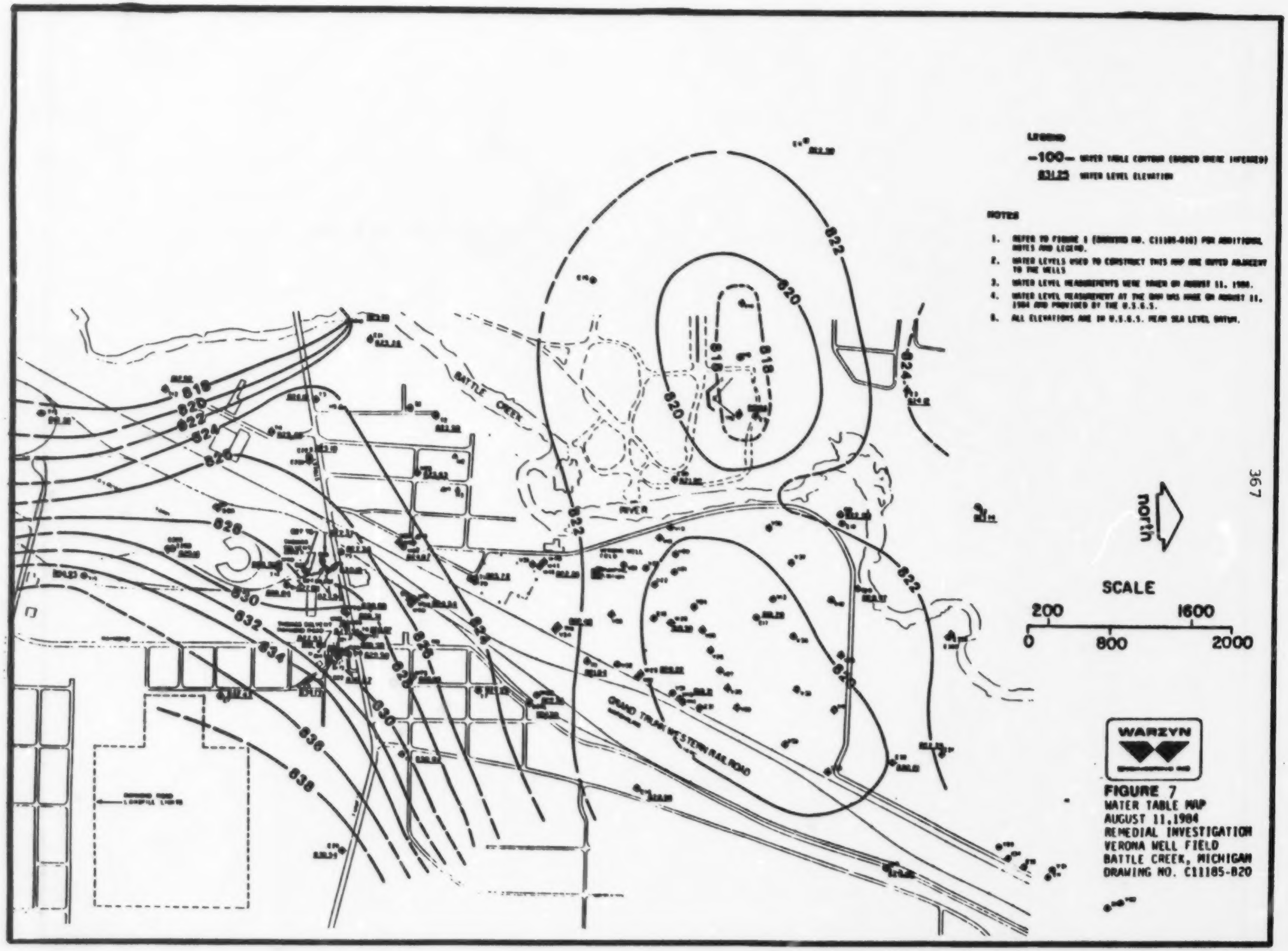

LEGEND
-100- WATER TABLE CONTOUR (DASHED WHERE INFERRED)
831.25 WATER LEVEL ELEVATION
NOTES
1. REFER TO FIGURE 1 (DRAWING NO. C11185-810) FOR ADDITIONAL NOTES AND LEGEND.
2. WATER LEVELS USED TO CONSTRUCT THIS MAP ARE NOTED ADJACENT TO THE WELLS
3. WATER LEVEL MEASUREMENTS WERE TAKEN ON AUGUST 11, 1984.
4. WATER LEVEL MEASUREMENT AT THE DAM WAS MADE ON AUGUST 11, 1984 AND PROVIDED BY THE U.S.G.S.
5. ALL ELEVATIONS ARE IN U.S.G.S. MEAN SEA LEVEL DATUM.
north
SCALE
0
200
800
1600
2000
WARZYN
818
820
822
824
826
828
830
832
834
836
838
BATTLE CREEK
RIVER
GRAND TRUNK WESTERN RAILROAD

FIGURE 7
WATER TABLE MAP
AUGUST 11,1984
REMEDIAL INVESTIGATION
VERONA WELL FIELD
BATTLE CREEK, MICHIGAN
DRAWING NO. C11185-820

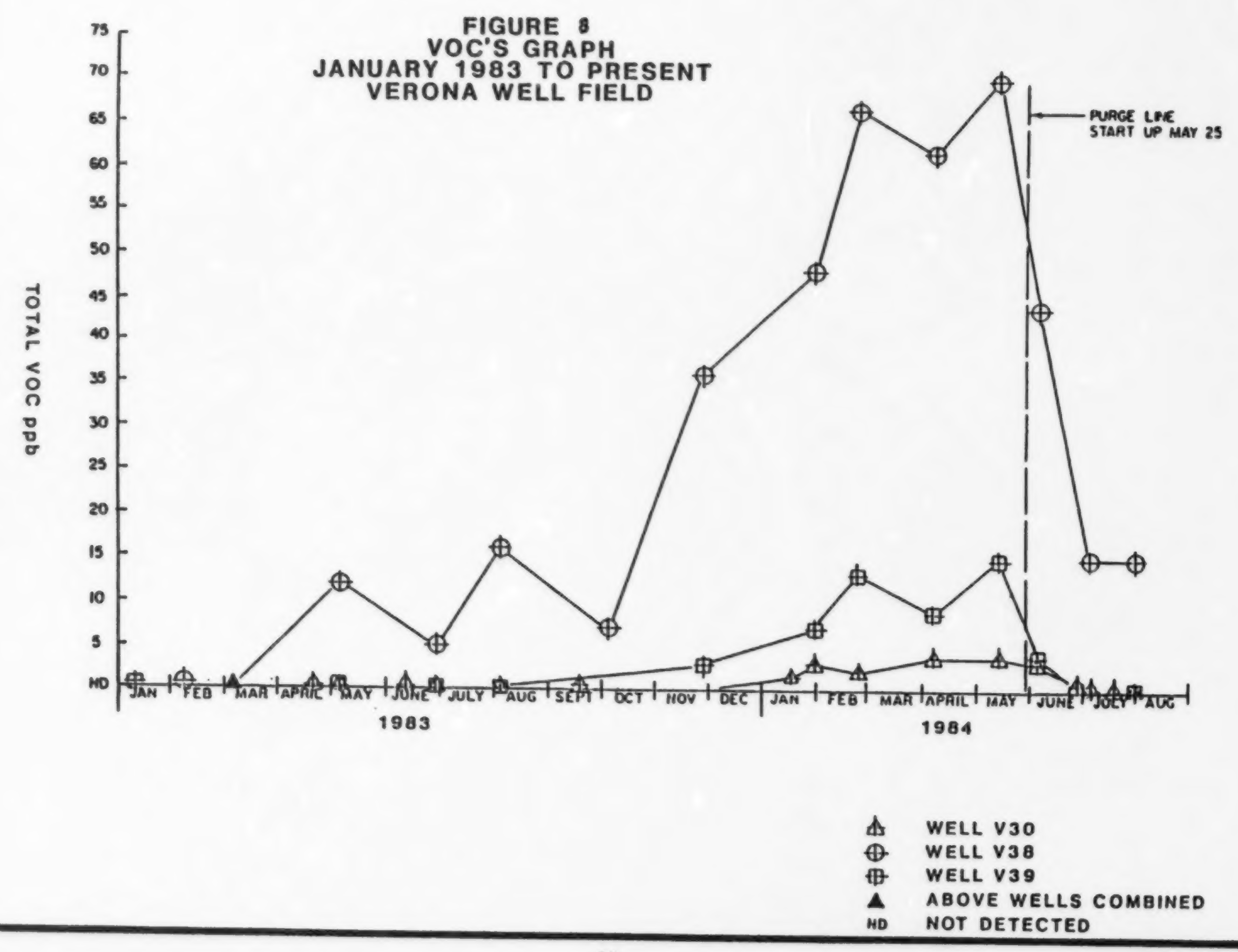


FIGURE 8
VOC'S GRAPH
JANUARY 1983 TO PRESENT
VERONA WELL FIELD

due to high levels of iron-reducing bacteria, excess volumes of carbon dioxide gas build up in the vessels due to reactions of the carbon with the high carbonate concentrations in the water, and uncharacteristic head losses across the carbon. Refitting the pumps with larger impellers to increase the head was a suggested solution which was rejected due to the cost and uncertainty of its actual effectiveness. Finally, it was agreed that regular backwashing of the carbon units would adequately control the problem. This measure would relieve any gas build-up on the units and also flush out any bacteria and/or silt accumulation on top of the vessels (Section 2.3).

3.2 RECOMMENDATIONS

For all large scale projects, an action plan should be developed before starting the work. The plan should briefly outline the proposed sequence of events, identify the critical elements, and be used to guide the project. Additionally, when dealing with water projects, basic water quality parameters should be obtained beforehand. This information is invaluable and necessary for the design of the system.

Unless there are problems with availability or delivery, a vertical turbine pump should be used instead of numerous small centrifugal pumps in parallel. This is not only economically more sound, but also a better engineered design. A single turbine pump will result in less excavation (no dry well would be required), less electrical switching, and less future maintenance. Use of a vertical turbine pump would also result in an above ground control room which would not only ease construction, but would also eliminate the problems of meeting OSHA and MIOSH health and safety standards for confined air spaces.

Being a construction rather than a cleanup project made this unique with respect to other Superfund Immediate Actions. While the ERCS contract is a very good concept, and an effective tool, it was primarily designed and written for use on hazardous waste cleanups. A revision of the contract, or possibly a new separate contract, should be considered for construction oriented actions. In the future, many Immediate Actions and IRM's will no longer be hazardous waste clean-ups; instead, many will be construction projects, and as such a revised ERCS contract, or a new construction ERCS contract would be very useful.

Stellako Spill

A Difficult Response Problem

by D.F. Brown[1] and A.C. Williams[2]

On August 8, 1984 at 23:39 hours a single vehicle accident occured on the approach to the Stellako River Bridge. The accident involved a tractor truck and trailer loaded with drums containing 100 kg of sodium cyanide pellets. Due to improper loading of the truck six drums fell off the truck. The local R.C.M.P. attended the scene and immediately contacted the Ministry of Environment and secured the scene. A.C. Williams, Environmental Safety Officer was notified of the spill at 23:47 hours and at this point he offered technical advise and took control of the spill cleanup. A.C. Williams prepared his truck and departed for Fraser Lake, 154 kilometres away. During the travelling period contact was maintained with the R.C.M.P., Fraser Lake detachment. Mr. Williams requested that the volunteer firemen standby and that spill cleanup materials be obtained. The R.C.M.P. with assistance from the local coordinator for the Provincial Emergency Program were able to procure all the materials and equipment required. Gathering these supplies would not have been possible without the cooperative spirit of the local businesses and industries.

The Village of Fraser Lake initially supplied eight volunteer firemen to work on the spill cleanup. These men were trained in the use of the S.C.B.A. but had no training in dealing with chemical spills. They were willing to assist in the cleanup but were very concerned about their personal safety.

A.C. Williams upon arriving at the spill site put on his protective gear and S.C.B.A. and toured the spill site. The purpose of the tour was to assess the extent of the problem and to demonstrate that the equipment protected him from danger. All six drums had broken open and the sodium cyanide pellets covered the road surface across the entire bridge as well as a significant area at the side of the road. It was obvious that a portion of what was spilled had entered the river. After the tour he met with all the firemen and explained the properties of sodium cyanide and operational cleanup methods. After the briefing session all the firemen were willing to work with A.C. Williams.

The firemen were formed initially into two teams, workers and back-up. The working group hand picked the area depositing the sodium cyanide pellets into barrels. The firemen were not assigned buddies as they were working a confined area. The safety of the workers was looked after by the back-up group. They observed all workers and were watching for problems. As the cleanup proceeded the Village of Fraser Lake dispatched an additional seven firemen to the site. With the additional help, the firemen were split into three groups; workers, back-up and a resting group.

A cyanide testing instrument was brought in from Endako Mines shortly after the cleanup commenced. The first pump on the test tube caused a complete color change. This indicated the ambient cyanide concentration was greater than 150 ppm approximately 60 cm above the road surface. After the majority of pellets were picked up the air was checked again for cyanide, the reading obtained was less than 10 ppm and at this time the S.C.B.A. were taken off. The initial cleanup continued for another five hours. The area was deemed to be safe and the highway was opened at 10:20, August 9, 1984.

Additional work done at the site revealed that a large number of cyanide pellets were buried in the road bank and concealed by heavy vegetation. As the emergency was past, the Ministry of Environment instructed the spiller to obtain expert help to continue the cleanup. In order to insure that the general public was not allowed access to the road banks, the Provincial Emergency Program maintained 24 hour surveillance of the site. The spiller hired Acres Consulting Services to complete the cleanup on August 10, 1984. The consultant organized a physical search of the area using local help and removed additional cyanide pellets. The initial cleanup by Acres was completed on August 11, 1984 and a total of 31 1/2 additional cyanide pellets were found. Ministry of Environment staff revisited the site on August 14, 1984. During this visit the first rainfall event subsequent to the spill occurred. The rain revealed many whole and broken pieces of cyanide pellets as it washed off the surface dust. Following this discovery the Ministry of Environment decided to excavate the top 15-20 cm from the road bank to insure all the cyanide was removed. On August 15, 1984 an hydraulic excavater was brought in from Prince George and the road bank was stripped of the top 15-20 cm of material. After this was completed the Ministry of Environment deemed the area to be clean. The spiller was instructed to erect warning signs describing the pellets and advising of the spill. No additional pellets were found at the site.

As with any spill a final disposal of the spilt material became a problem. This was resolved by having a local mine at Endako take the waste cyanide and excavated materials. The mine was able to recycle the cyanide into its process and arrange for the excavated gravel to go to the waste tailing pond.

The spill of cyanide at the Stellako River bridge had the potential of being extremely serious. The Stellako River is the source of drinking water for a large mobile home park. The water intake was immediately downstream of the bridge. This water supply was shut off and water was trucked in. The intake was not started up until the Environmental Laboratory reported the cyanide in the river as non detectable. The Stellako River flows into Fraser Lake approximately 1.4 kilometres from the bridge. A further 2.6 kilometres along the shore of the lake is the water intake for the Village of Fraser Lake. Detectable concentrations of cyanide were found in the water samples taken at depth over the intake. On the west side of the Stellako River is a very large Indian reservation. At the time of the spill three men from the reserve were on the bridge and they were showered with the pellets. These men were taken to a motel and were examined by a local doctor. He advised that the men should shower extensively and their clothing should be destroyed.

The recreational resource of the Stellako River is of great value. It is considered to be one of the finest rainbow trout fisheries in British Columbia. In addition the Stellako River supports a large salmon run. The salmon run was not expected for two weeks; therefore, the spill did not impact this run.

The time of day also helped to minimize the human problems. Highway 16 is extremely busy during the day at this time of the year with tourist traffic. Fortunately the tourists were off the road by the time of the spill and as such were unaffected.

In order to protect the public and help reduce fears a joint press release was issued by the Ministries of Health and Environment. The press release notified the public of the spill and advised that water from the Stellako River-Fraser Lake should not be consumed until test results were obtained. The analytical results indicated that cyanide was present but within the drinking water standards.

The spill of cyanide had little effect on the receiving environment. This was due to the rapid response of the Environmental Safety Officer in arranging for a cleanup. Had weather conditions been different the potential for death was extremely large. During the entire spill cleanup period it rained only once. Through leadership and education, A.C. Williams was able to make effective use of the volunteer firemen in cleaning up the spilt cyanide pellets. The company that transported the cyanide and the shipper who authorized the load were charged under the Federal Fisheries Act and the Waste Management Act. The company plead guilty to the first charge and was fined eight thousand dollars. The Waste Management Act charges were stayed by the Crown. In sentencing the company the Judge stressed that death and damage to the environment was prevented by the rapid response of all the agencies involved.

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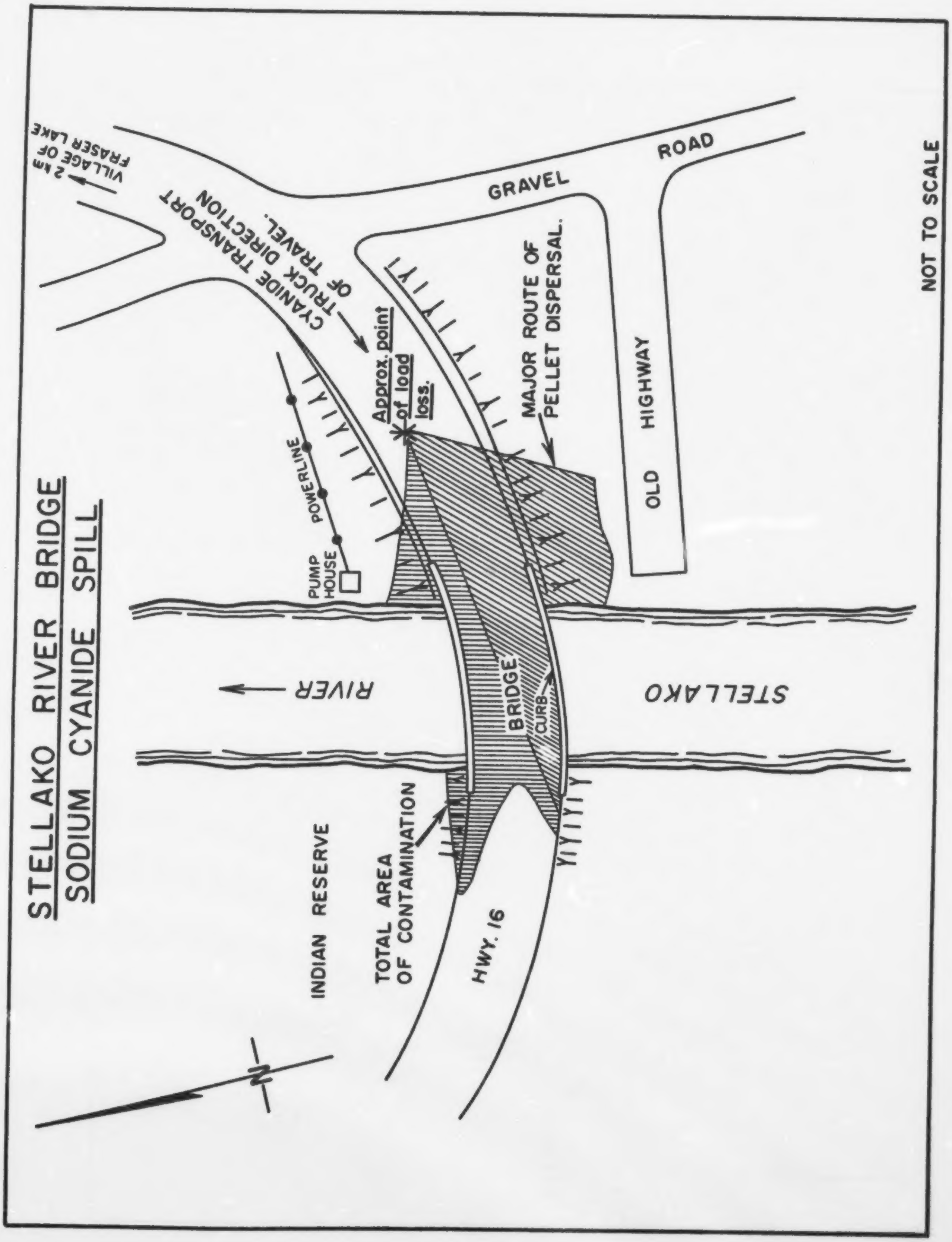
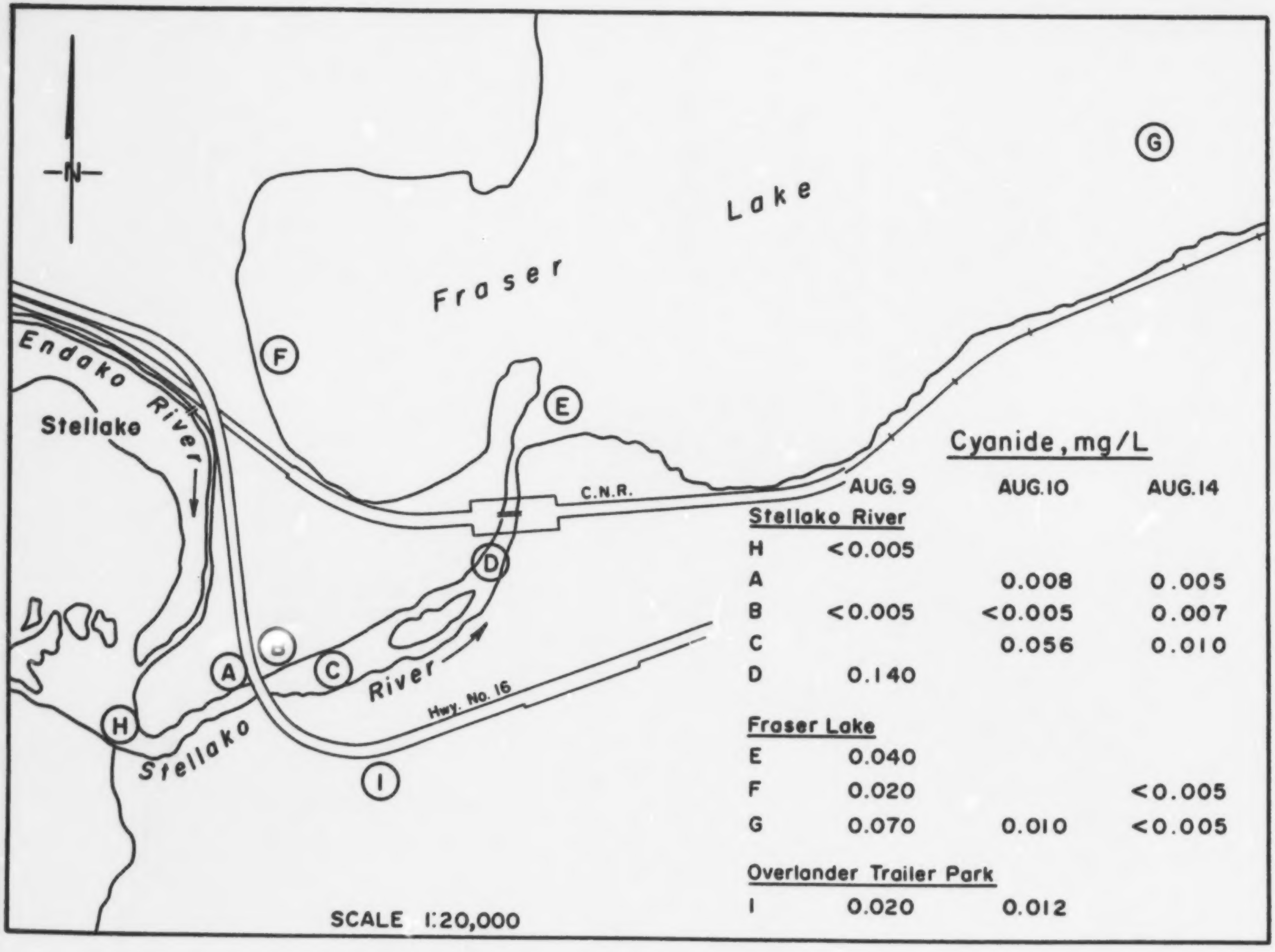

STELLAKO RIVER BRIDGE
SODIUM CYANIDE SPILL
2 km
VILLAGE OF FRASER LAKE
CYANIDE TRANSPORT TRUCK DIRECTION OF TRAVEL.
GRAVEL ROAD
Approx. point of load loss.
MAJOR ROUTE OF PELLET DISPERSAL.
OLD HIGHWAY
NOT TO SCALE
POWERLINE
PUMP HOUSE
RIVER
STELLAKO
BRIDGE
CURB
TOTAL AREA OF CONTAMINATION
INDIAN RESERVE
HWY. 16
N


N
Fraser Lake
Endako River
Stellake
Stellako River
C.N.R.
Hwy. No. 16
A
B
C
D
E
F
G
H
I
SCALE 1:20,000

Cyanide, mg/L

	AUG. 9	AUG. 10	AUG. 14
Stellako River			
H	<0.005		
A		0.008	0.005
B	<0.005	<0.005	0.007
C		0.056	0.010
D	0.140		
Fraser Lake			
E	0.040		
F	0.020		<0.005
G	0.070	0.010	<0.005
Overlander Trailer Park			
I	0.020	0.012	

WARNING

A spill of Sodium Cyanide Pellets occurred at this bridge on Aug. 8, 1984. Anyone who sees anything resembling a white charcoal briquette or a piece of one should leave it alone and notify the RCMP, Fraser Lake detachment.

INNOVATIVE TECHNOLOGY FOR THE RECOVERY OF ORGANIC CONTAMINANTS FROM GROUND WATER -- WITH TWO CASE STUDIES.

By

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ABSTRACT

The removal of immiscible organic contaminants from a ground-water aquifer generally requires pumping wells 12 inches in diameter or greater. Removal or recovery is performed by utilizing a submersible water well pump to create a "cone of depression" and a petroleum recovery or "scavenger" submersible pump to recover the free phase contaminant. Each pump is equipped with sensors which discriminate between petroleum and water.

A new dual pump recovery system has been designed with modifications to ensure efficient recovery in 4 to 6 inch diameter pumping wells. This system can pump water up to 60 gpm. It can recover water-free immiscible organics up to a depth of 200 feet. The utilization of this system is more cost effective and efficient due to the greater availability and lower costs associated with drilling smaller diameter wells.

Two case studies describe the use of this system in two different applications. The first was used in a coastal aquifer of moderate transmissivity. The system was deployed to contain and recover a 100,000 gallon jet fuel spill. The second was deployed with a water treatment/recharge system to remove free and dissolved petroleum contamination from a high yield aquifer. The restoration of the aquifer was required to prevent contamination of a nearby municipal water supply well.

(a) Presently with E.R.M. Northeast
Boston, Mass.

INTRODUCTION

The recovery or removal of free phase petroleum products or solvents from ground water aquifers has been successfully accomplished for a period of years by deploying two-pump, recovery systems in pumping wells with a minimum diameter of twelve inches (30 cm) to 36 inches (91 cm). The availability of drilling rigs with the capability to install a 12" to 36" diameter well can be restrictive in many areas. The expense and lack of availability of larger diameter well materials can further add to the difficulty of recovery well installation (especially to depths greater than 40 feet).

Six-inch diameter wells are the standard for the water well industry. Most water well drillers are familiar with the techniques and materials involved in the installation of a six-inch water well. To that end, the availability of a dual pump petroleum recovery/water table depression system with the capability for installation in a four to six-inch diameter recovery well is a versatile, cost effective alternative to the larger more difficult to install recovery wells. The cost effectiveness of such a system is increased if the relative costs involved are comparable to a Standard Scavenger Pump and Water Table Depression Pump.

The Dual Pump Scavenger System is a single compact system which recovers free phase product while simultaneously depressing the water table. The unique dual pump configuration allows deployment in a small diameter (4" to 6") well. The system operates at depths as great as 200' and requires less than 1 inch of product for recovery.

The product pump is a positive displacement, self-priming pump capable of recovering 1000 gpd over 100' deep. Construction materials are stainless steel and Teflon for long wear and corrosion resistance.

The water pump is a 1/2 HP stainless steel submersible turbine pump capable of 28 gpm output flow at depths of over 100'. Options include flow rates to 50gpm and a 150' discharge head.

The dual pump controls are mounted in an explosion proof, weather tight panel for use in Class 1, Division 1, Groups C and D areas. Indicators depict the status of product and water pumps and recovery tank level. The Scavenger Controller is designed for secure and inconspicuous deployment below ground or in an adjacent building (Refer to Figure 1).

This pumping system has been deployed successfully in Canada and throughout the United States. The following is a discussion of two of these investigations in two very different environments. The first is in a high yield glacial aquifer with relatively small amounts of leaked petroleum in a environmentally sensitive area. The second is in a man made aquifer of moderate transmissivity with large amounts of leaked hydrocarbon in an area of potential coastal impacts.

INVESTIGATION I

The first site is situated above a high yield glacial aquifer in the geographic center of a small New England Community located 1/4 mile upgradient from a lake which feeds a municipal water system. The site is an independently owned service station which had been in operation for a period of 30 years. During a routine site assessment performed as part of the purchase and sales agreement, subsurface petroleum contamination was detected in two monitoring wells. Two unleaded and one super unleaded underground storage tanks were tested by the Petro-Tite tank testing method. The two unleaded tanks did not test tight having a leaking rate of -0.99 gallons per hour far exceeding the 0.05 gallons/hour criteria. As a result of this testing the unleaded tanks were drained and subsequently removed. (Refer to Figure 2).

Methods of Investigation

A total of seven monitoring wells were drilled on and around the site. The first two were drilled under the direction of a local engineering firm. The next five were installed under the direction of Groundwater Technology. Each well was completed using 2-inch diameter schedule 40 PVC slotted well screen. These wells were installed to define the physical characteristics of the aquifer sediments, groundwater flow characteristics and the areal extent of groundwater contamination.

Split-spoon samples were taken at two to five foot increments to document the geologic profile of aquifer sediments in each well. Geologic logs were prepared for each monitoring well. Each monitoring well was constructed of two inch diameter schedule 40, .020 slotted PVC screen with two inch diameter PVC casing. Each well was screened through the water table to allow free-floating gasoline, if present in the aquifer, to enter the well. Clean natural backfill was emplaced around the screen and casing to a depth of one foot below grade. No artificial gravel pack was required because of the coarse, granular natural of the in-situ soils. A bentonite seal was set around the top of each well as protection from surface water contamination. All the wells were capped with cast iron road boxes.

Each of the monitoring wells were developed by bailing and surging to remove formation plugging and ensure adequate hydraulic communication to the aquifer. Each monitoring well was surveyed to determine the top of casing elevation to a fixed datum.

Upon completion each monitoring well was gauged from the top of well casing to determine depth to water and presence or absence of free-floating petroleum. Measurements were made with an Electronic Interface Probe which utilizes optical and conductivity sensors. This Probe can detect the depth to water and thickness of free-floating petroleum phases with an accuracy of 1mm. By analysis of the formation, groundwater elevations, flow direction and the extent of hydrocarbon contamination were determined. Figure 3 depicts groundwater flow under nonpumping conditions. Groundwater Flow is West-Northwest across the site.

Chemical Analyses

Groundwater Technology collected a free-floating gasoline sample from Monitoring Well # 2. It was analyzed for percent lead to determine whether the gasoline was leaded or unleaded.

To assess the extent and concentration of dissolved petroleum contamination in the aquifer the groundwater was analyzed from six observation wells in accordance with EPA method 602 for dissolved hydrocarbons in water. It is imperative that this procedure be performed to define the leading edge of the contaminant plume.

Although petroleum products are generally immiscible with water, they do contain some constituents, which are slightly solube. The most soluble are the aromatic compounds such as benzene, toluene, ethyl benzene and xylenes. Samples were collected by removing a minimum of three well volumes of water from each well to obtain representative water samples. Samples from each well were collected in duplicate in 40 ml VOA septum vials. The samples were refrigerated and properly preserved and chain of custody procedures were followed to ensure quality control.

Based upon the results of the initial water quality analyses, a Dissolved Hydrocarbons in Water Map was prepared (Figure 4). The Comparison of static Groundwater Flow and Contaminant Plume Maps Figures 3 & 4 showed a dissolved and free-floating hydrocarbon plume migrating from a point source. Based upon this information, a recovery well was located in the center of this plume.

Recovery Well Design, Installation and Development

The recovery well was constructed using a mud rotary drilling rig. The well was designed with 20 feet of wire-wrapped low carbon steel Irrigator screen with a solid bottom plate. The diameter of the screen was 6 inches and the slot opening was .050 inches based upon split spoon sample grain size analyses. A recovery well was drilled and completed to a depth of 48 feet.

The annular space between the screen and the bore hole was filled with natural backfill. This was chosen based on analysis of sediment grain size distribution curves from sediment sieve analyses.(1) These samples were derived from split spoon samples collected during monitoring well drilling which indicated that natural backfill was coarse grained with little fine material.

Development of the well removed formational plugging and fine-grained material from the natural soils. A cable tool drilling rig, outfitted with a double block agitator performed the development procedures. The agitator was moved slowly up and down throughout the screened portion of the recovery well for 2 days. During the agitation procedure, water in the well was being bailed out, removing finer grained material brought into suspension by the development. This action developed a natural gravel pack around the well screen.

An eight hour pumping test was performed to determine the characteristics of the aquifer. This pumping test, determined the aquifer's transmissivity to be very high at 250,000 gallons per day per foot. The natural velocity of groundwater flow was calculated to be 2 ft/day. This is the rate at which groundwater moved beneath the site under non-pumping conditions. This rate is fast, however free-floating hydrocarbons have been found to flow up to 10 times slower than groundwater. Consequently the natural velocity of contaminants is reduced to 0.2 ft/day.

Transmissivity:	250,000 gpd/ft
Hydraulic Conductivity:	5,000 gpd/ft^2
Groundwater Velocity:	2 ft/day

The values are for non-pumping conditions. The recovery well water table depression will alter the natural rate of groundwater flow. (Refer to Figure 5)

Recovery System Design and Installation

The petroleum recovery well operation consists of a dual pump system: an Oil Recovery Systems Probe Scavenger/Water Table Depression Pump (WTDP). The WTDP is equipped with controls so that it selectively pumps only water to create a cone of depression in the groundwater. The Prove Scavenger System is specially designed with controls to detect petroleum products and evacuate the petroleum as it accumulates in the well.

Groundwater Discharge

The recovery well was designed to discharge water through a solid 4-inch PVC pipe to an air stripping water treatment unit at a flow rates varying from 50 to 100 gallons per minute. Groundwater contaminated with dissolved hydrocarbons will be removed of volatile organics such as benzene, ethyl benzene, toluene, xylenes, aliphatic and aromatic hydrocarbons typical of gasoline. The volatile organics are removed from the water by cascading contaminated water down a packed 3-foot diameter column counter-current to a relatively large volume of air, supplied by an air blower unit. Influent & effluent water quality samples were taken and analyzed in accordance with guidelines set by local Environmental officials to determine the water treatment efficiency.

Aquifer Recharge

The majority of the treated groundwater was discharged to a 4-inch perforated PVC pipe into two parallel 50-foot long infiltration trenches.

A smaller 2-inch pipe tapped into the air stripper discharge and directed some of the treated groundwater to an infiltration gallery near the tank area. This enhanced groundwater restoration by flushing the soil in the suspected source area of the leak. Groundwater from both infiltration trenches was recharged hydraulically upgradient to the groundwater flow direction. The action of the recovery well pumping and groundwater recharge increased the hydraulic gradient and thus the flow of groundwater, speeding the removal of petroleum contamination from the site.

By implementation of the dual pump/recharge system, the concentrations of dissolved hydrocarbons were reduced by 90% in a 30 day period. Furthermore, - 1000 gallons of free-phase gasoline were recovered over nine months of operations (Refer to Figure 6).

INVESTIGATION II

The second site is located at a coastal airport site in the Atlantic Provinces of Canada. The sit is underlain by a moderate to high yield man-made aquifer. The project was undertaken in response to a line leak spilling 100,000 gallons of jet fuel under the parking apron at the airport.

Site Assessment

Initially, a site assessment was performed and data from nine existing monitoring wells were collected and analyzed. These wells were installed by another consulting firm prior to Groundwater and Oil Recovery Systems' involvement. Top of casing elevation for each well was surveyed by using a rod and transit. Direction of groundwater flow and distribution of free-floating hydrocarbons were determined from this data. The presence of significant amounts of free-floating hydrocarbon indicated the necessity of emplacing additional monitoring wells to further define the area of contamination.

Monitoring Well Construction and Development

Eight additional Monitoring Wells (MW-10 through MW-17) were installed to further define the area of contamination. The locations of these wells are shown in Figure 7.

Each well was drilled using the Air Rotary Drilling Method. The boreholes were 6-inch diameter and drilled to a depth of approximately 25-feet. MW-17 was drilled to a depth of 37 feet to document the lower boundary of the aquifer. Each well was completed using the same methods described in Investigation I.

According to airport personnel, a clay barrier was installed beneath the sand and gravel by the U.S. Army during airport construction. The clay barrier was not penetrated during drilling thus preventing cross contamination between upper and lower aquifers.

Groundwater elevations and hydrocarbon distribution data was collected from these wells. Based upon the analyses of this date, three additional monitoring wells were installed using the same methods and depths as Monitoring Well 10 through 17. Each well was then surveyed into a fixed datum (MW-1) to determine water table elevations. Groundwater flow under static condition is to the Southwest towards the ocean. The distribution of free-floating hydrocarbon indicated migration parallel to groundwater flow direction form a point source. (Refer to Figures 7 & 8).

Recovery Well Design, Installation and Development

The recovery well was located near the center of the free-floating hydrocarbon plume. This location was selected after analysis of monitoring well data. Significant amounts of free-floating hydrocarbons were detected in the vicinity of MW-10, MW-11 and MW-17. The recovery well, being situated downgradient from leak location, permits recovery of any free-floating hydrocarbons within the area of influence created by recovery well pumping.

Well screen type and slot size were selected based on grain-size analyses performed on sediment samples obtained during monitoring well construction. The recovery well was constructed with 25 feet of 6-inch diameter, 25 slot wire wound irrigator well screen with a bottom plate.

A 10 foot section fo blank 6-inch steel casing was welded on the top of the well screen. The annular space between the borehole and well screen was packed with native fill to a depth of 1 foot where a bentonite seal was installed to prevent infiltration of surface water run-off. Upon completion, the recovery well was developed by bailing and surging using a 5-inch diameter bailer.

Aquifer Testing

An aquifer pumping test was performed on Recovery Well #1. The testing was performed by pumping the well continuously at a fixed flow rate. The water levels in the pumping well and surrounding monitoring wells were measured periodically for the duration of the test. The rate and amount of decline in water levels at the surrounding wells were recorded for analysis.

Hydraulic parameters such as transmissivity, well efficiency and area of influence can be determined by analysis of the aquifer test data. Based on the analysis of the data, the optimum pumping rate was determined and the correct water pump was chosen to optimize petroleum recovery.

The pumping test determined the aquifer's transmissivity to be moderate to high at 100,500 gallons per day per foot. The natural velocity of groundwater flow was calculated to be 4.3 ft/day. This is the rate at which groundwater moves beneath the site under non pumping conditions. This flow rate is relatively fast for groundwater flow. However, it should be noted that free-floating hydrocarbons will not migrate at this rate. We have found that petroleum tends to flow up to 10 times slower than groundwater. Consequently the natural velocity of petroleum migration may be reduced to 0.43 ft/day.(2)

Transmissivity:	100,500 gpd/ft
Hydraulic Conductivity:	3865 gpd/ft^2
Groundwater Velocity:	4.3 ft/day

The values are for non-pumping conditions. The recovery well water table depression will alter the natural rate of groundwater flow. (Refer to Figure 9).

Equipment Installation

Based on data analysis, the dual pump recovery system capable of installation in a 6-inch diameter recovery well was chosen. The system consists of a 2hp stainless steel Water Table Depression Pump and a petroleum recovery pump. Each pump being controlled by separate electronic probes.

Water discharge was piped using 1 1/2 inch diameter schedule 40 blank iron pipe installed in a trench routing it through the 6-inch aviation gas line (not in use) at hydrant #1. At this point, it is connected to a 2-inch flexible discharge hose placed inside the 6-inch aviation gas line to the pit located in the pump crib. From the pit the discharge line ties back to 2-inch schedule 40 black iron pipe above grade that discharges the water into the nearby stream.

The product recovery line follows the same flow path to the crib using 1/2 inch schedule 80 black iron pipe from the recovery well to the fueling hydrant. At this point it connects to a 1-inch petroleum discharge hose to the pump crib where it discharges into a 2-inch diameter schedule 40 black iron pipe. This pipe runs along th north fence perimeter to the pump house for final discharge to tank #4. This tank has a storage capacity of 40,000 imperial gallons. Electrical power is supplied from the pump cribs electrical panel by conduit to the 4-inch diameter conduit used for the dead man controls to hydrant #1 (the same path as the discharge piping to Recovery Well #1).

Hydrocarbon Distribution

The extent of hydrocarbon contamination under non-pumping conditions is depicted in Figure 8. It shows the apparent free-floating hydrocarbons as lines of equal thickness. The plume is elongated parallel to the direction of groundwater flow (325 feet x 100 feet). The maximum thickness of the plume is +3.0 feet.

After sixty-two days of pumping operation changes in petroleum distribution were observed as depicted in Figure 10. Fourteen of the monitoring wells show a decrease in hydrocarbon thickness and apparently the leading edge of the hydrocarbon plume down-gradient has been drawn back towards the recovery well. However, based on our capture zone and stagnation point calculations, all petroleum more than 56 feet downgradient of the well will not be drawn back to the well. As of October 10, 1985 approximately 16,000 imperial gallons of jet fuel has been recovered.

Conclusions

These two case histories demonstrate the effectiveness of the small diameter dual pump recovery system in two vastly different applications. The first case study shows the effectiveness of the dual pump system in recovering small quantities of free-floating product while removing and treating high concentrations of dissolved hydrocarbons from the groundwater. The effectiveness of the system prevented contamination from reaching a municipal water well. The second case study depicts the systems ability to recover large quantities of free-floating hydrocarbons in a moderately permeable aquifer. The effectiveness allowed the recovery of a reusable ressource and prevented migration of the contaminant plume from impacting fertile fishing beds on the coast.

References

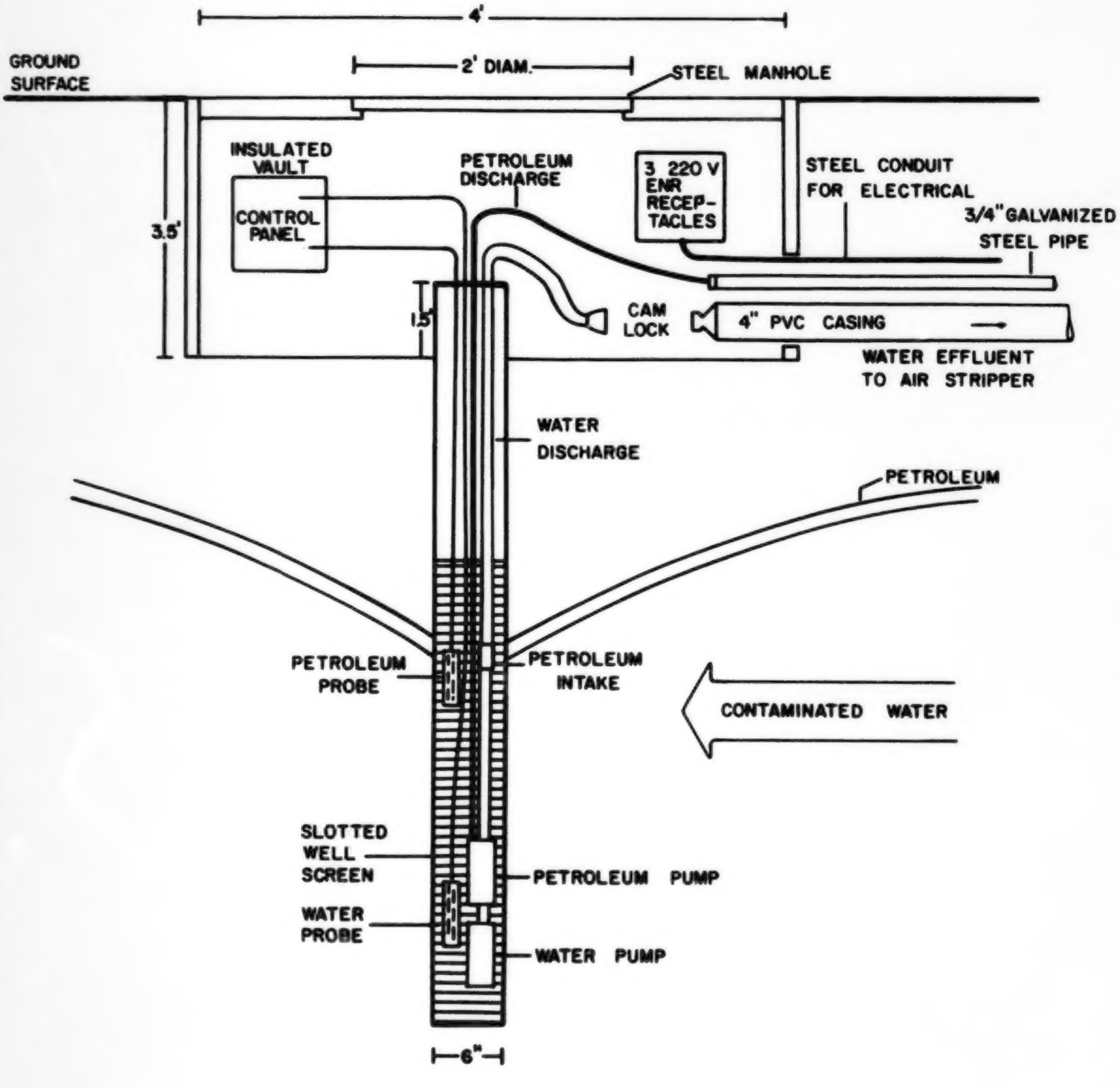
1) ASTM STANDARD D422063. Determination of Grain Size via Dry Sieving.

2) Cooper, H.H., Jr. and C.E. Jacob, "A Generalized Graphical Method of Evaluation Formation Constants and Summarizing Well Field History". Trans AM Geophysical Union, Vol. 27, pp. 524 and 526 Washington.

FIGURE I

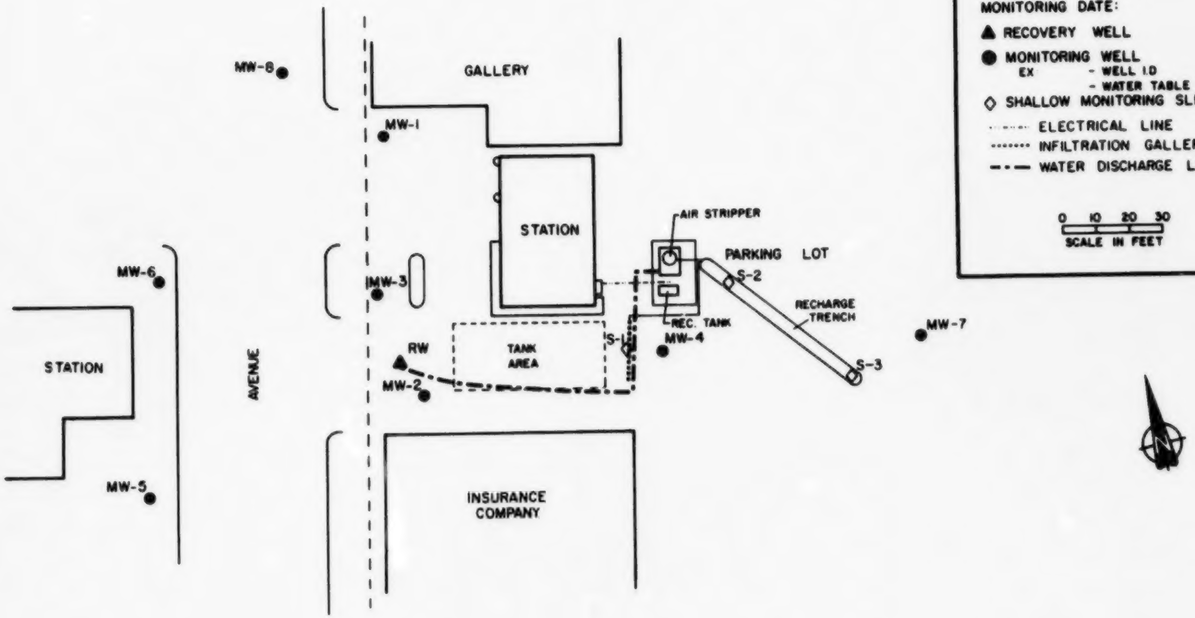
RECOVERY WELL ENCLOSURE

DUAL PUMP SYSTEM SCHEMATIC


4'
2' DIAM.
GROUND SURFACE
STEEL MANHOLE
INSULATED VAULT
CONTROL PANEL
3.5'
PETROLEUM DISCHARGE
3 220 V ENR RECEP-TACLES
STEEL CONDUIT FOR ELECTRICAL
3/4" GALVANIZED STEEL PIPE
1.5'
CAM LOCK
4" PVC CASING
WATER EFFLUENT TO AIR STRIPPER
WATER DISCHARGE
PETROLEUM
PETROLEUM PROBE
PETROLEUM INTAKE
CONTAMINATED WATER
SLOTTED WELL SCREEN
PETROLEUM PUMP
WATER PROBE
WATER PUMP
6"

GROUNDWATER TECHNOLOGY

FIGURE 2


MW-8
GALLERY
MW-1
STATION
AIR STRIPPER
PARKING LOT
S-2
RECHARGE TRENCH
MW-7
MW-6
MW-3
REC. TANK
S-1
MW-4
S-3
STATION
AVENUE
RW
TANK AREA
MW-2
MW-5
INSURANCE COMPANY
N

SITE MAP

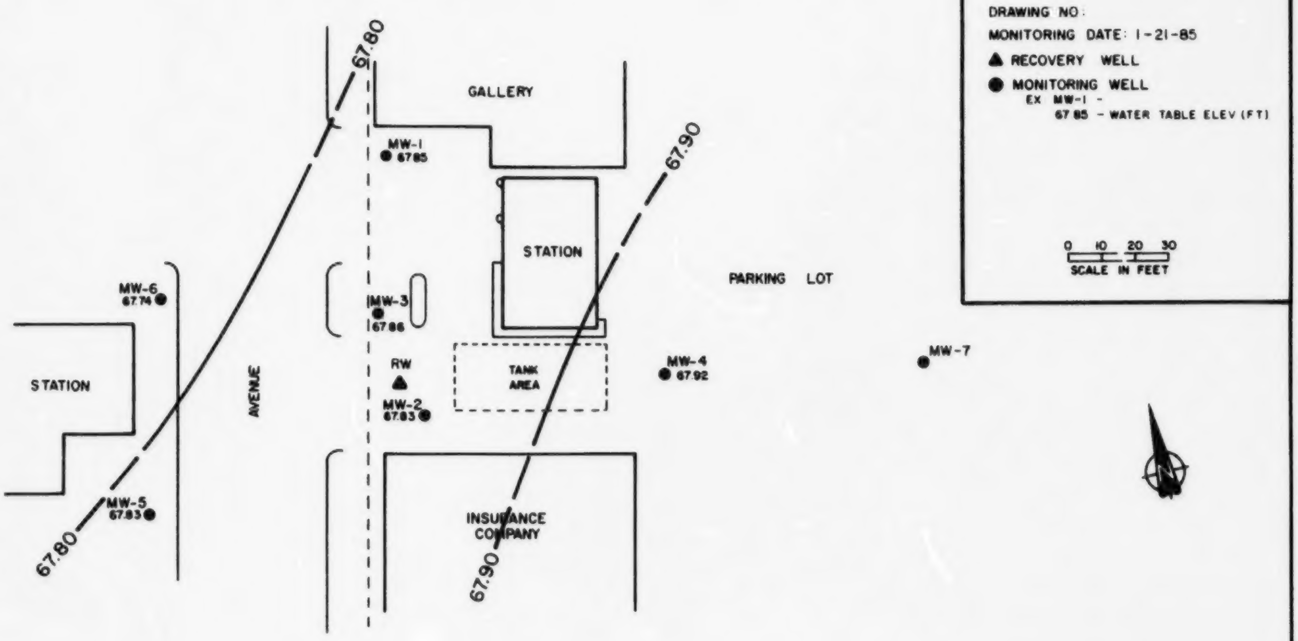
DRAWING NO: 10-3813-1
MONITORING DATE:
▲ RECOVERY WELL
● MONITORING WELL
EX - WELL I.D
- WATER TABLE ELEV.(FT.)
◇ SHALLOW MONITORING SLEEVE
-·-·- ELECTRICAL LINE
······· INFILTRATION GALLERY
-·— WATER DISCHARGE LINE

0 10 20 30
SCALE IN FEET

GROUNDWATER
TECHNOLOGY

FIGURE 3

GROUNDWATER CONTOUR MAP
STATIC CONDITIONS


DRAWING NO:
MONITORING DATE: 1-21-85
▲ RECOVERY WELL
● MONITORING WELL
EX MW-1 -
67.85 - WATER TABLE ELEV (FT)
0 10 20 30
SCALE IN FEET
67.80
67.90
GALLERY
STATION
TANK AREA
INSURANCE COMPANY
PARKING LOT
AVENUE
STATION
MW-1 67.85
MW-2 67.83
MW-3 67.86
RW
MW-4 67.92
MW-5 67.83
MW-6 67.74
MW-7

GROUNDWATER TECHNOLOGY

DISSOLVED HYDROCARBONS OVER TIME

FIGURE 4

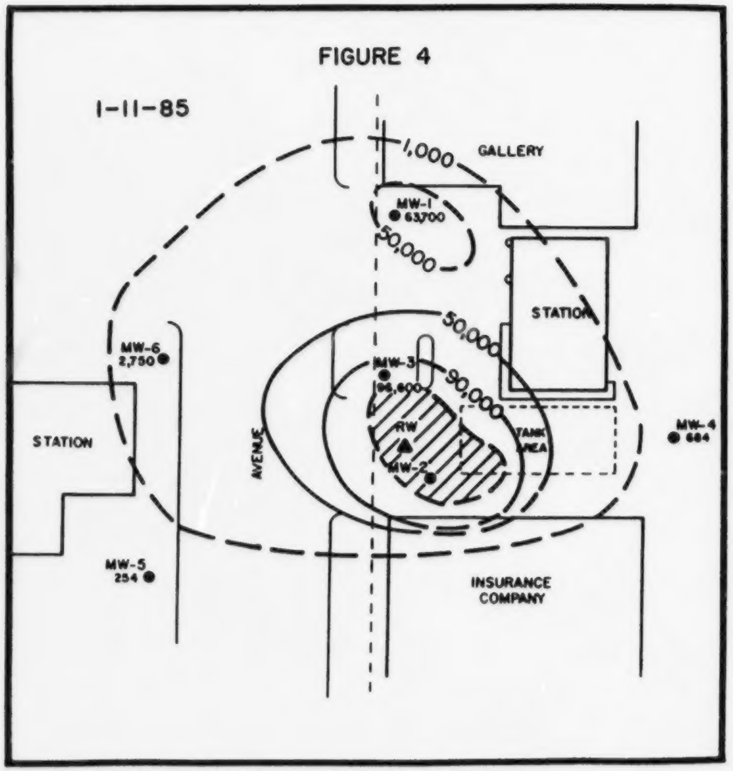
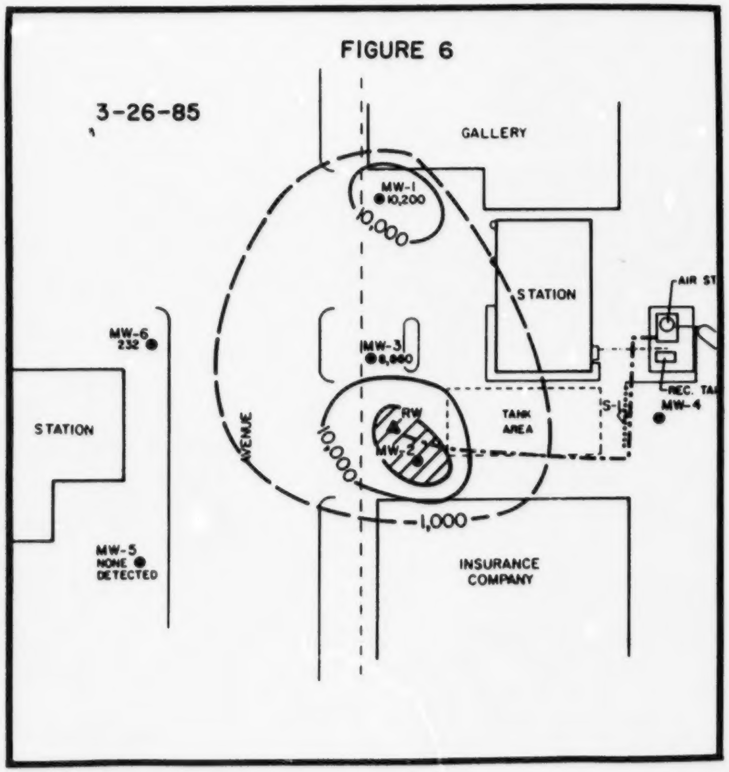
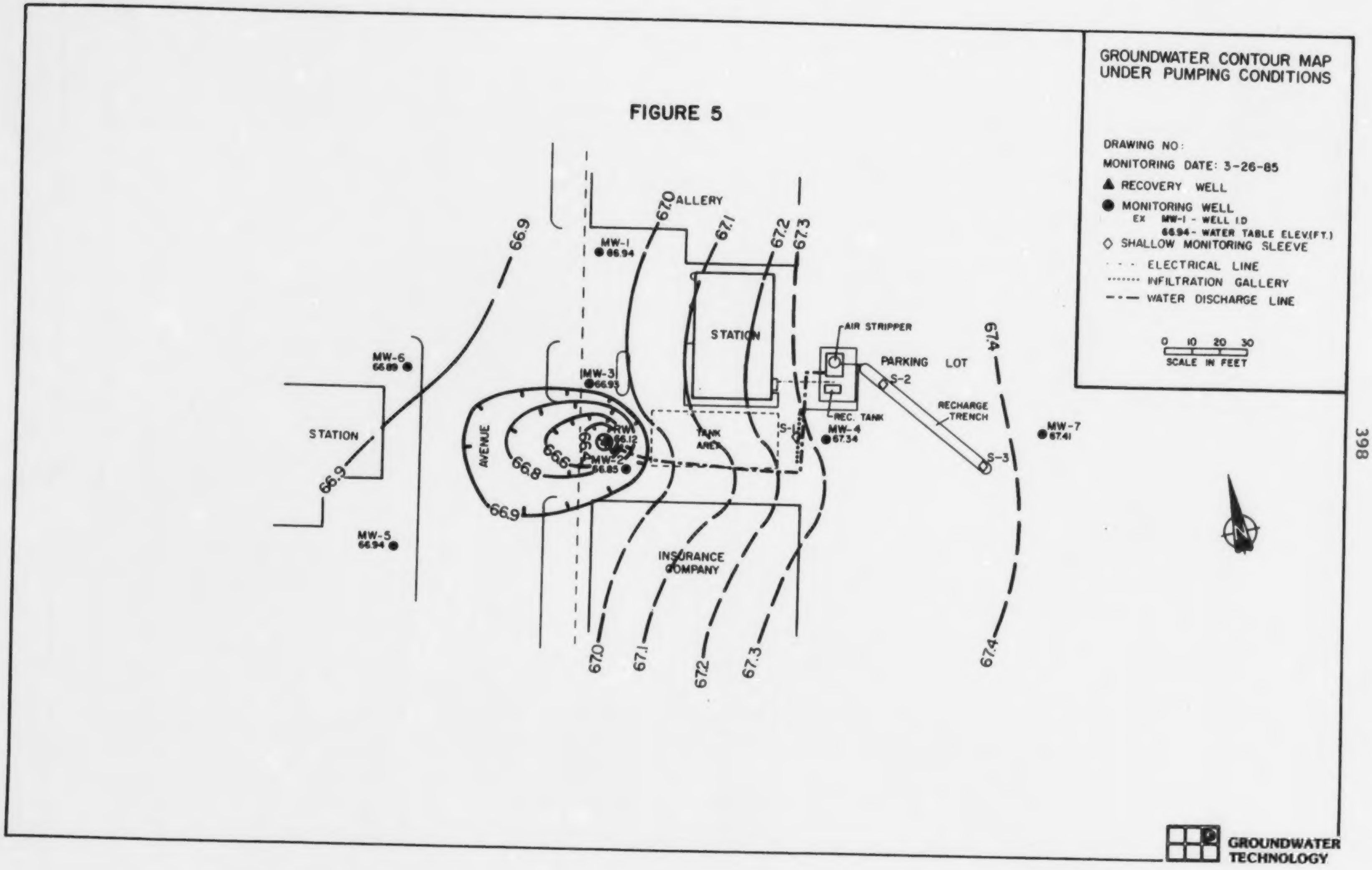

1-11-85
GALLERY
STATION
STATION
TANK AREA
AVENUE
INSURANCE COMPANY
1,000
50,000
50,000
90,000
MW-1 63700
MW-3 96,600
RW
MW-2
MW-4 684
MW-6 2,750
MW-5 254

FIGURE 6


3-26-85
GALLERY
STATION
STATION
TANK AREA
AVENUE
INSURANCE COMPANY
AIR ST
REC. TA
S-1
10,000
10,000
1,000
MW-1 10,200
MW-3 8,900
RW
MW-2
MW-4
MW-6 232
MW-5 NONE DETECTED

GROUNDWATER
TECHNOLOGY

FIGURE 5


GALLERY
STATION
TANK AREA
PARKING LOT
AIR STRIPPER
REC. TANK
RECHARGE TRENCH
S-1
S-2
S-3
MW-1 66.94
MW-3 66.93
RW 66.12
MW-2 66.85
MW-4 67.34
MW-5 66.94
MW-6 66.89
MW-7 67.41
AVENUE
STATION
INSURANCE COMPANY
66.6
66.8
66.9
66.9
67.0
67.1
67.2
67.3
67.4
N

GROUNDWATER CONTOUR MAP
UNDER PUMPING CONDITIONS

DRAWING NO:
MONITORING DATE: 3-26-85
▲ RECOVERY WELL
● MONITORING WELL
EX MW-1 - WELL I.D.
66.94 - WATER TABLE ELEV.(FT.)
◇ SHALLOW MONITORING SLEEVE
- · - · ELECTRICAL LINE
······· INFILTRATION GALLERY
— · — WATER DISCHARGE LINE

0 10 20 30
SCALE IN FEET

GROUNDWATER TECHNOLOGY

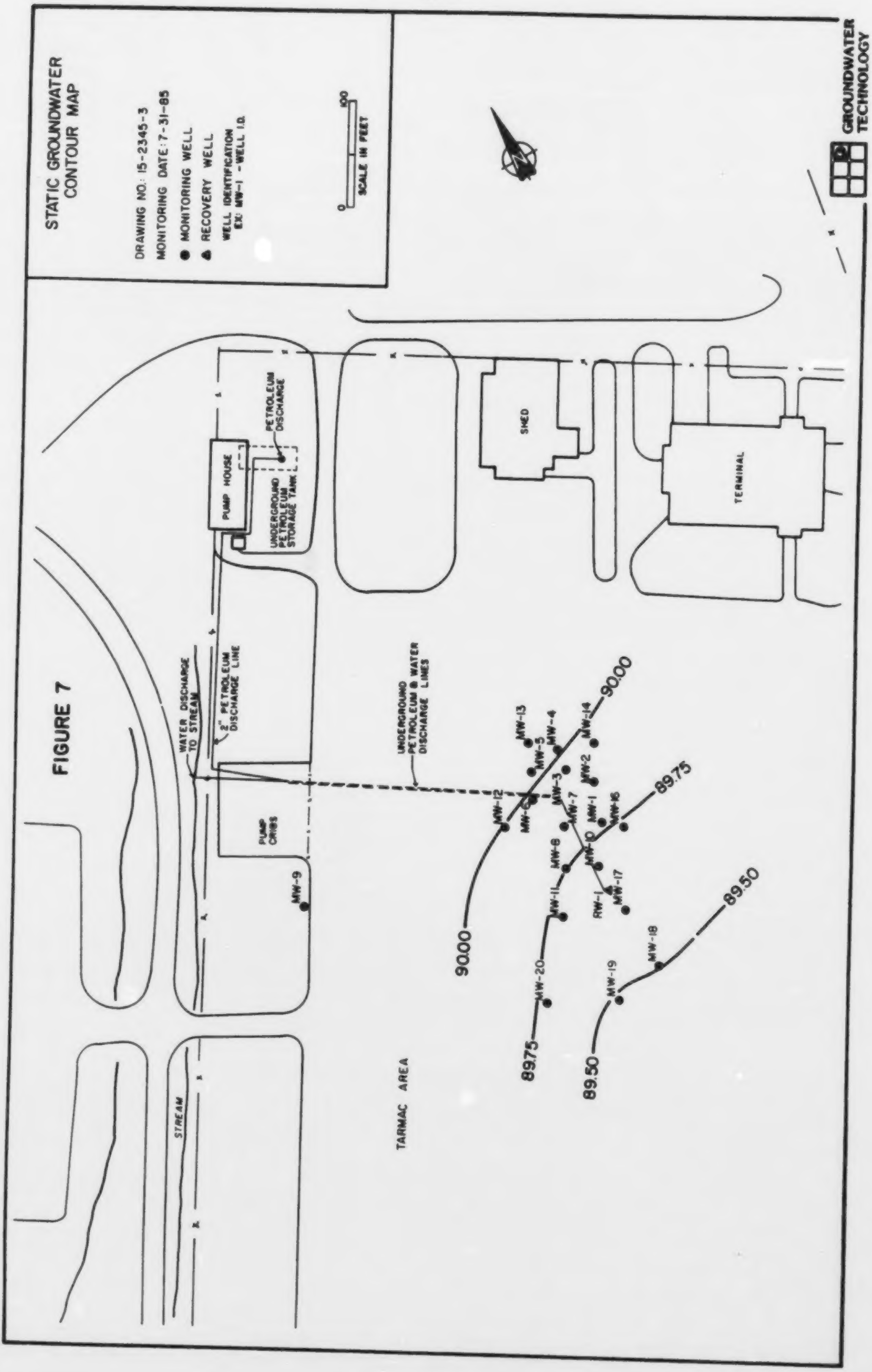
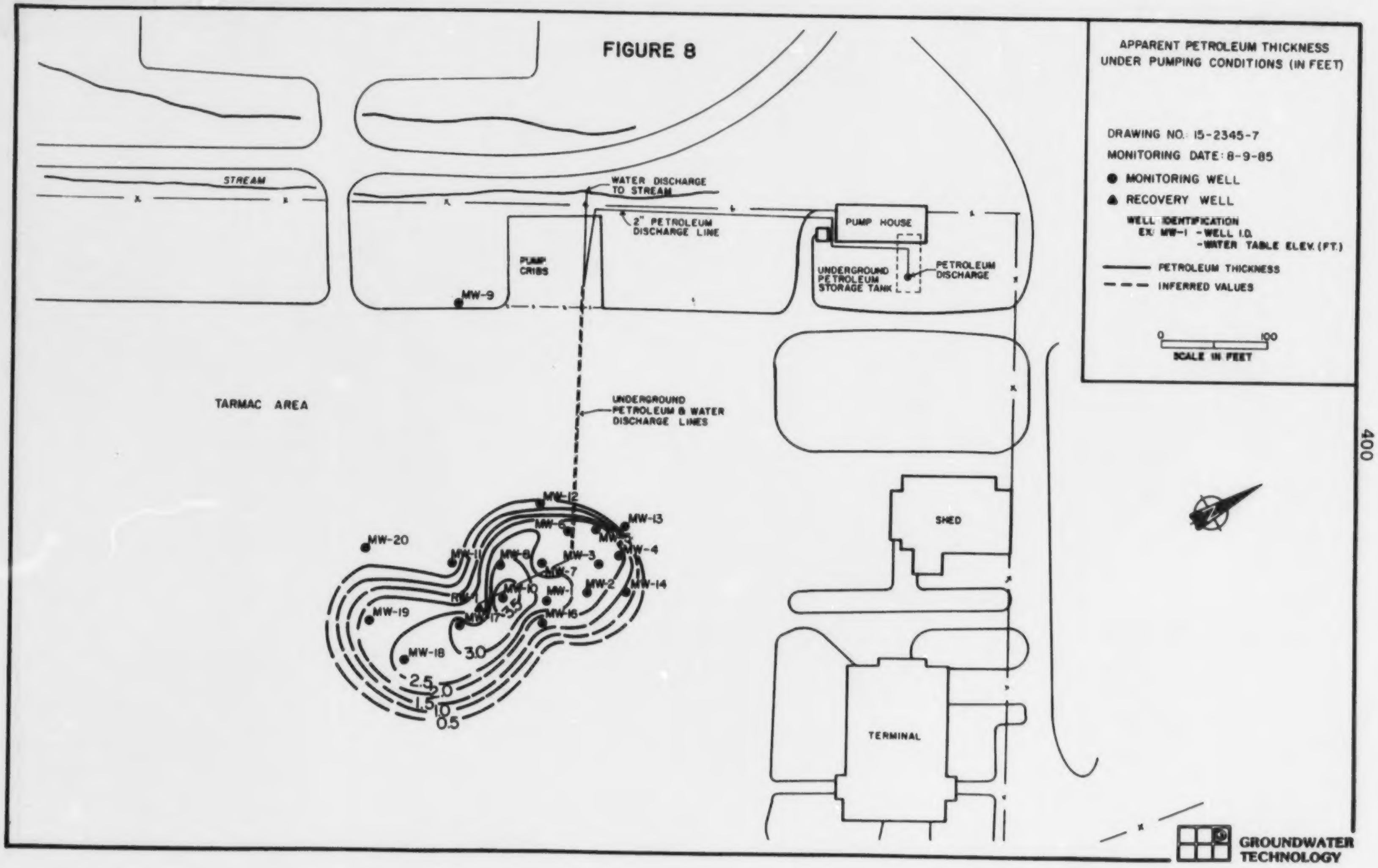


FIGURE 7

STATIC GROUNDWATER CONTOUR MAP

DRAWING NO.: 15-2345-3
MONITORING DATE: 7-31-85
● MONITORING WELL
▲ RECOVERY WELL
WELL IDENTIFICATION EX: MW-1 - WELL I.D.
0
100
SCALE IN FEET
GROUNDWATER TECHNOLOGY
PUMP HOUSE
PETROLEUM DISCHARGE
UNDERGROUND PETROLEUM STORAGE TANK
SHED
TERMINAL
WATER DISCHARGE TO STREAM
2" PETROLEUM DISCHARGE LINE
UNDERGROUND PETROLEUM & WATER DISCHARGE LINES
PUMP CRIBS
STREAM
TARMAC AREA
MW-1
MW-2
MW-3
MW-4
MW-5
MW-6
MW-7
MW-8
MW-9
MW-10
MW-11
MW-12
MW-13
MW-14
MW-16
MW-17
MW-18
MW-19
MW-20
RW-1
90.00
90.00
89.75
89.75
89.50
89.50

FIGURE 8


APPARENT PETROLEUM THICKNESS
UNDER PUMPING CONDITIONS (IN FEET)
DRAWING NO. 15-2345-7
MONITORING DATE: 8-9-85
● MONITORING WELL
▲ RECOVERY WELL
WELL IDENTIFICATION
EX: MW-1 - WELL I.D.
-WATER TABLE ELEV. (FT.)
PETROLEUM THICKNESS
INFERRED VALUES
0
100
SCALE IN FEET
STREAM
WATER DISCHARGE TO STREAM
2" PETROLEUM DISCHARGE LINE
PUMP HOUSE
PUMP CRIBS
UNDERGROUND PETROLEUM STORAGE TANK
PETROLEUM DISCHARGE
MW-9
TARMAC AREA
UNDERGROUND PETROLEUM & WATER DISCHARGE LINES
MW-12
MW-13
MW-6
MW-5
MW-4
MW-20
MW-11
MW-8
MW-3
MW-7
MW-10
MW-1
MW-2
MW-14
RW-1
MW-17
MW-16
MW-19
MW-18
3.5
3.0
2.5
2.0
1.5
1.0
0.5
SHED
TERMINAL
GROUNDWATER TECHNOLOGY

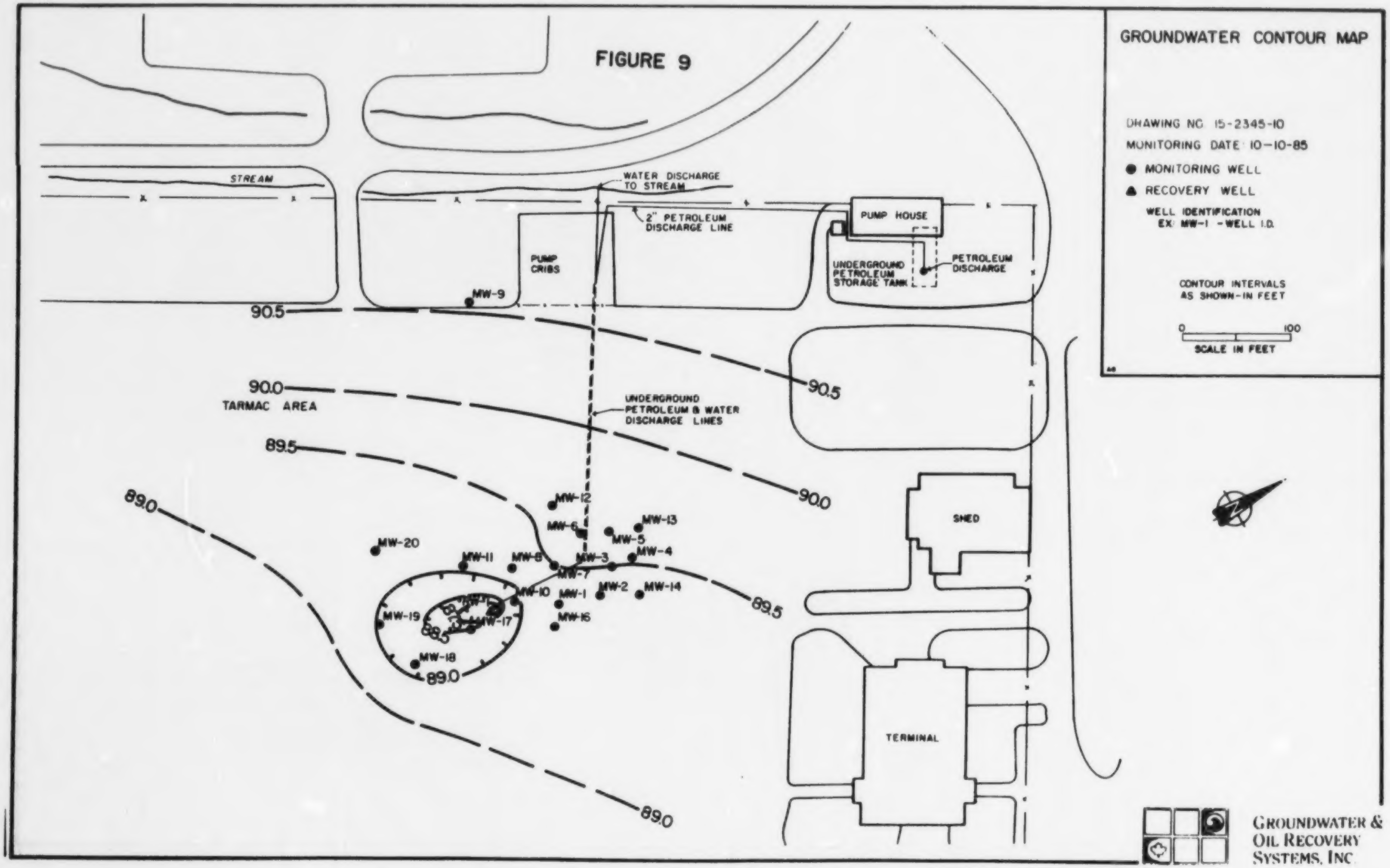


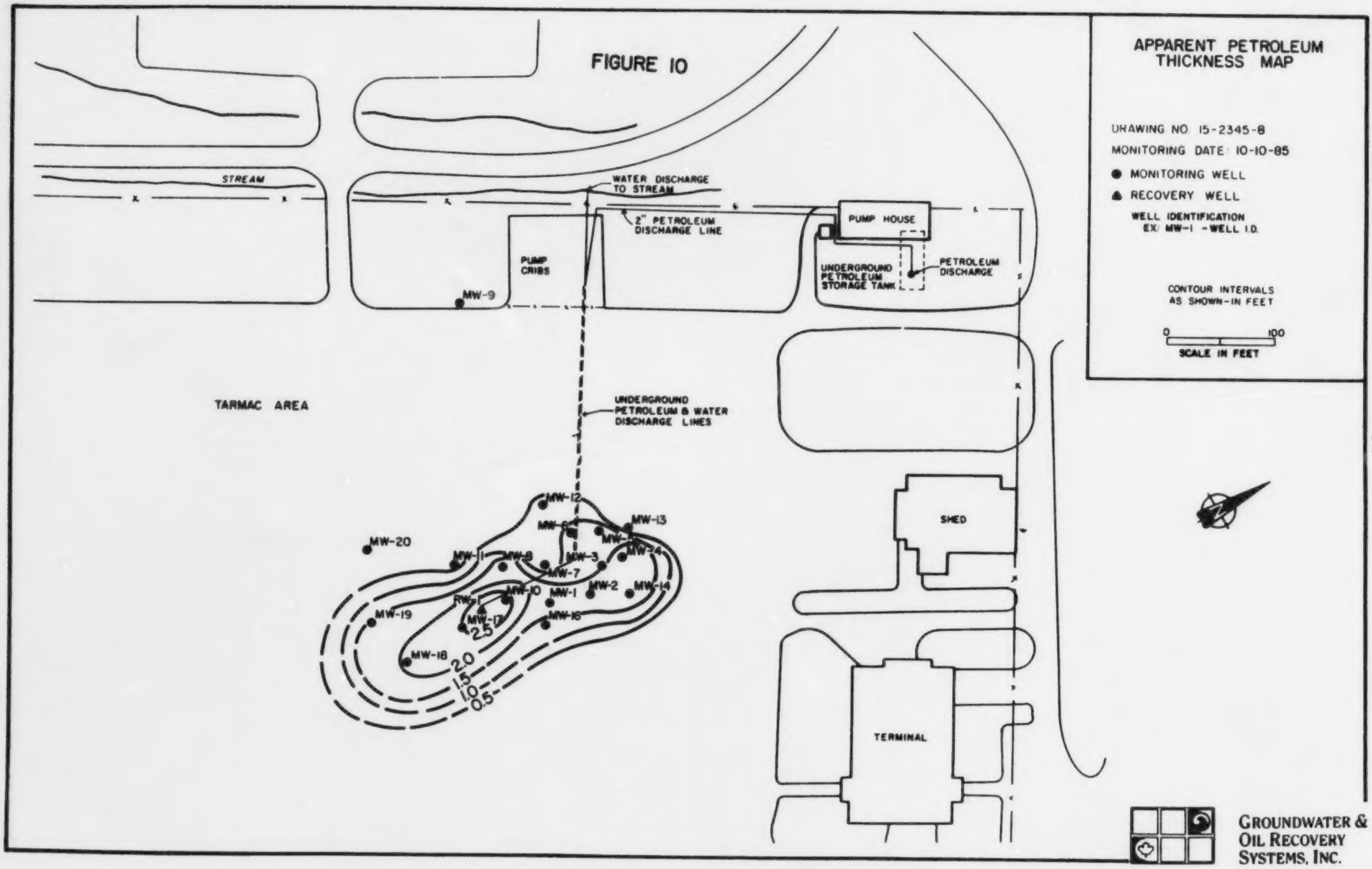
FIGURE 9

GROUNDWATER CONTOUR MAP

DRAWING NO. 15-2345-10
MONITORING DATE: 10-10-85
● MONITORING WELL
▲ RECOVERY WELL
WELL IDENTIFICATION EX: MW-1 - WELL I.D.
CONTOUR INTERVALS AS SHOWN-IN FEET
0
100
SCALE IN FEET
STREAM
WATER DISCHARGE TO STREAM
2" PETROLEUM DISCHARGE LINE
PUMP HOUSE
UNDERGROUND PETROLEUM STORAGE TANK
PETROLEUM DISCHARGE
PUMP CRIBS
MW-9
90.5
90.5
90.0
TARMAC AREA
UNDERGROUND PETROLEUM & WATER DISCHARGE LINES
90.0
89.5
89.5
89.0
89.0
89.0
88.5
MW-12
MW-13
MW-6
MW-5
MW-4
MW-20
MW-11
MW-8
MW-3
MW-7
MW-10
MW-1
MW-2
MW-14
MW-19
MW-17
MW-16
MW-18
SHED
TERMINAL

GROUNDWATER &
OIL RECOVERY
SYSTEMS, INC

FIGURE 10


APPARENT PETROLEUM THICKNESS MAP
DRAWING NO. 15-2345-8
MONITORING DATE: 10-10-85
● MONITORING WELL
▲ RECOVERY WELL
WELL IDENTIFICATION EX: MW-1 - WELL I.D.
CONTOUR INTERVALS AS SHOWN-IN FEET
0
100
SCALE IN FEET
STREAM
WATER DISCHARGE TO STREAM
2" PETROLEUM DISCHARGE LINE
PUMP HOUSE
UNDERGROUND PETROLEUM STORAGE TANK
PETROLEUM DISCHARGE
PUMP CRIBS
MW-9
TARMAC AREA
UNDERGROUND PETROLEUM & WATER DISCHARGE LINES
MW-12
MW-13
MW-3
MW-7
MW-4
MW-11
MW-8
MW-10
MW-1
MW-2
MW-14
RW-1
MW-17
MW-16
MW-19
MW-18
MW-20
2.5
2.0
1.5
1.0
0.5
SHED
TERMINAL
N
GROUNDWATER & OIL RECOVERY SYSTEMS, INC.

THE USE OF PHOTOIONIZATION DETECTION INSTRUMENTS IN HAZARDOUS SPILL EVALUATION

INTRODUCTION

Instruments using Photoionization Detection (PID) technology are finding increasing application in the analysis of air, groundwater and soil and gas analysis in the vicinity of hazardous spills. It is important that these instruments be portable, rugged, reliable and produce both qualitative and quantitative analysis with a minimum of operator skill. Recent advances in PID miniaturization combined with the use of micro computers have come a long way towards meeting these stringent requirements. Current field investigations are based on a two stage strategy which requires the use of a hand held "Total Ionizables" instrument in combination with a fully automated portable Gas Chromatograph (G.C.).

Photoioniztion Detection

The detector consists of a lamp, filled with low pressure gas, which is excited by radio frequency energy "coupled" into the gas through a coil which surrounds the body of the lamp (Figure 1). Extremely short wavelength ultraviolet (UV) light is emitted from the lamp and this has a photon energy which is typically about 11 eV. The principle of operation makes use of the fact that the majority of permanent gases and most of the common air gases cannot be photoionized by 11 eV radiation but the vast majority of organic gases and vapors, and a few inorganics, can be photoionized.

Thus, if pure air passes through a cell which is irradiated with UV, there will be no photoionization. If the air contains an organic impurity, such as benzene vapor, this will be ionized and the ions can be detected using a collection electrode connected to a very sensitive amplifier.

This fortunate property is of tremendous value in pollution analysis.

Total Ionizables Present (TIP) Instruments

These instruments are designed to utilize the PID's ability to distinguish pollutants from air gases and thus provide a simple evaluation of the total pollutant burden in the air. The criteria for choosing a TIP instrument for a particular mission involve the following considerations:

- portability
- ease of use
- sensitivity
- linearity
- reliability
- effect of humidity

The general configuration of this type of instrument is illustrated in Figure 2. An internal pump draws the air sample through the detector and the "TIP" level detected is displayed on a digital readout. The instrument is powered by rechargeable batteries mounted in the handle section and the pump should have sufficient capacity to draw air to the detector via a particulate filter, so as to prevent coating of the lamp window. The capability exists for attachment of extended probes, which are important for measuring difficult access areas such as the bottom of bore holes. Technical specifications for this type of instrument are shown in Figure 3.

It is important to realize that TIP instruments do not effectively distinguish between different pollutants. When only one compound is present or a mixture of constant composition, the TIP instrument can be calibrated to read directly in ppm. If a chaotic mixture exists, the instrument can be used as a valuable indicator of total burden -- preparatory to more precise qualitative measurements.

Calibration of these instruments is best carried out using a standard of the particular compound under scrutiny. In field conditions, a relative response factor is frequently used as a practical means of calibration. A single compound is chosen as the primary calibrant and data are translated for other compounds using a table such as Figue 4.

In some spill situations it is necessary to obtain identification and quantitative results for the compounds present, in order to augment the TIP findings. Alternatively, it may be desirable to measure extremely low contamination levels. For these cases, portable photoionization gas chromatographs have been developed.

Portable PID Gas Chromatographs

These instruments can yield spectacular sensitivity. For example, benzene, from gasoline spills, has been detected down to levels as low as 0.1 ppb for a 1 mL sample volume and with a 4:1 signal-to-noise ratio. Our group has been successful in developing a new type of PID which is capable of detecting such compounds as chloromethanes, chloroethanes and even fluorochloromethanes, which were not previously amenable to this technique.

Our portable GC (Figure 5) can perform fully automated air sampling by combining an integral air pump with a series of computer controlled three-way solenoid valves. With this arrangement, a wide range of different chromatographies are possible which include auto sampling with software selectible sample volume, auto calibration, precolumn/backflush and even multicolumn arrangements. As an illustration, Figure 6 shows a typical configuration.

Automatic identification and quantitation can be achieved using four built-in libraries, each one having a 25-compound capacity. The computer also monitors column temperature, battery charging and provides an automatic baseline zero at the commencement of each analysis. A typical output from the built-in printer/plotter is shown in Figure 7. Computer functions are all controlled by a simple keyboard or, alternatively, an auto-dial modem used in conjunction with an RS 232 output enables both output data and input control commands to be transmitted through telephone lines to home base.

The major advantage in using portable GCs is the speed with which high quality data can be obtained. This capability now enables field personnel faced with a problem situation to take on-the-spot remedial action decisions based on facts. The timely evaluation, control and clean-up of spill situations may now be conducted in a safer and more cost-effective manner.

The use of Total Ionizables Present and portable PID GCs for hazardous spill investigations has been well documented (1), (2), (3), (4), (5), (6), and (7).

Field Experience and Case Studies

It is an unfortunate fact of life that each spill situation is different and therefore the method of evaluating and solving the problem will be different. It is thus impossible to establish rigid criteria for evaluating the problem and conducting any remedial action. Similarly the individual role for both TIPs and GCs, where their use is indicated, will vary in each case but some general guidelines can be established for the stages of action.

Stage 1 - Initial Response

Using TIP, initial data are obtained to establish protection levels for worker health and safety, document potential hazard to the general public, and to evaluate the overall extent of the area involved and the estimated environmental impact of the incident. Set-up priorities for mitigation activies.

Stage 2

Use GC to verify TIP data from Stage 1. Use TIP and GC to set up site boundaries to prevent public access, identify potential sampling points. Establish site work zones for various levels of protection for operatives.

Stage 3

Use GC and TIP to generate data under different meteoroligical conditions to provide detailed evaluation of the degree and extent of contamination from the incident with a minimum of the delay and expense which occurs when samples are collected for laboratory analysis. TIP, GC and laboratory analysis are used in combination to determine the full extent of air, groundwater and soil gas contamination. The US EPA Environmental Response Team have developed a method for rapidly sampling for volatile organics in shallow soil profiles. This technique may be used to identify and measure the vapors from both spills and underground tank leaks.

Stage 4

Data can be used to determine and evaluate mitigation activities. Real-time monitoring during remedial actions will allow for the evaluation of on-going respiratory protection for personnel and the effectiveness of the clean-up performance during the operation can be concluded.

Stage 5

During hydrogeological investigations, the data can be used for the development of depth versus contaminant concentration profiles and the prevention of accidental well contamination.

Stage 6

Evaluate and document the overall effectiveness of the operation.

Conclusion

The use of portable photoionization instruments for hazardous spill evaluation has significantly increased in recent years due to:

improved instrumentation,

development of field techniques,

acceptance of the technology,

increased experience of the benefits of this approach.

The driving force for this change has been a combination of financial and safety factors which are likely to continue to gain in importance.

- cost of savings due to a reduction in laboratory analysis.

- cost savings due to minimal delay in obtaining factual data to start remedial action.

- worker and public safety is improved by real-time measurements.

- worker and public safety is also improved because low cost multiple sampling allows a more thorough analysis of the situation to be available to the clean-up team at all stages of the operation.

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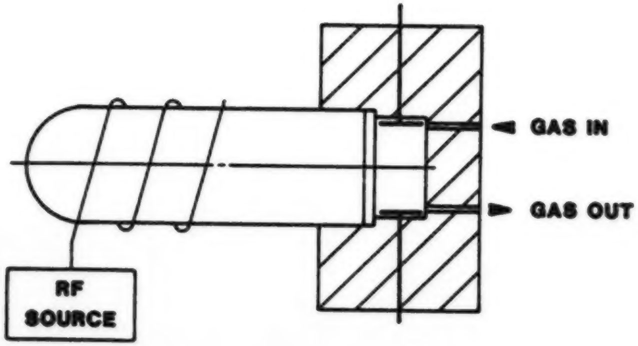
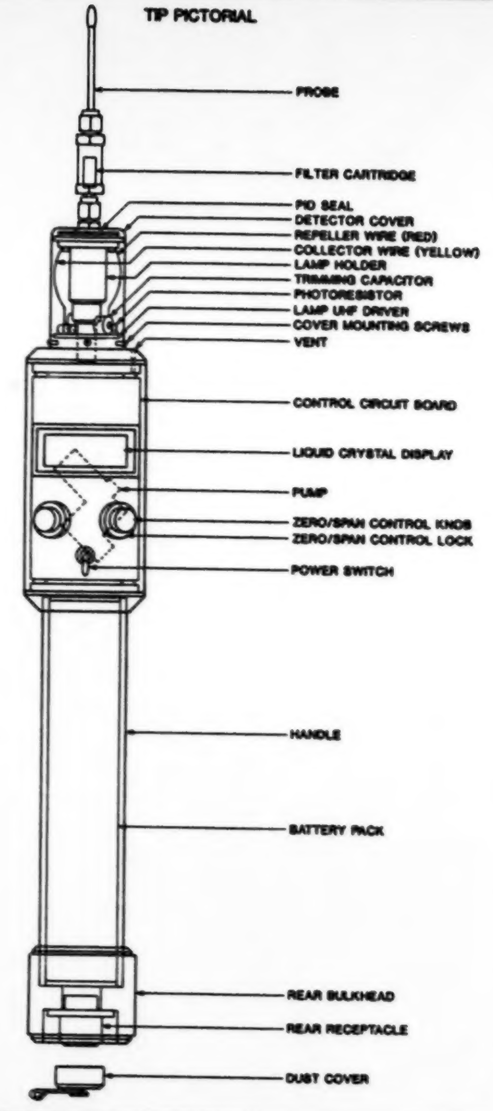
Figure 1


GAS IN
GAS OUT
RF SOURCE

REGULAR PHOTOVAC®
SINGLE CHAMBER DETECTOR

Figure 2


TIP PICTORIAL
PROBE
FILTER CARTRIDGE
PID SEAL
DETECTOR COVER
REPELLER WIRE (RED)
COLLECTOR WIRE (YELLOW)
LAMP HOLDER
TRIMMING CAPACITOR
PHOTORESISTOR
LAMP UHF DRIVER
COVER MOUNTING SCREWS
VENT
CONTROL CIRCUIT BOARD
LIQUID CRYSTAL DISPLAY
PUMP
ZERO/SPAN CONTROL KNOB
ZERO/SPAN CONTROL LOCK
POWER SWITCH
HANDLE
BATTERY PACK
REAR BULKHEAD
REAR RECEPTACLE
DUST COVER

GENERAL

Size	45 cm (18") long 6.3 cm (2.5") diameter (maximum)
Weight	1.5 Kg (3 lbs) approximately
Detector type	Photoionization, 10.6 eV UHF excited electrodeless discharge tube
Safety approvals	Applications pending

PNEUMATIC

Inlet flowrate	275 mL/min approximately
Inlet fitting	1/8" stainless steel Swagelok™
Inlet filter	15 μm replaceable stainless steel cartridge

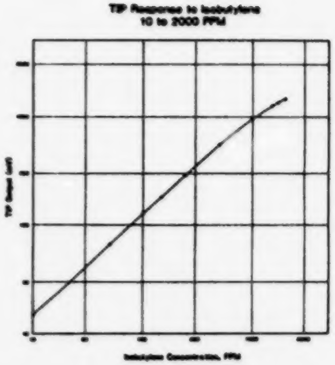
ELECTRICAL

Display	3 1/2-digit liquid crystal (0.0 to 1999 counts), illuminated
Battery type	NiCd
Charge/discharge time	16 hr/4 hr approximately; charger provided
Low battery indication	at 95% discharge
Signal outputs	1 Volt FS, analog concentration, and modulated pulse for external (optional) earphone
External power	12 Volt DC, 0.4 A. (***TIP*** ° has internal regulation)

PERFORMANCE

Range	0 — 2000 ppm
Detection limit	0.05 ppm (benzene)
Linearity	0 — 100 ppm, ±10% 100 — 1000 ppm, ±15% (see chart)
Response time	3 sec (10% to 90% FS, 10 ppm benzene)
Precision	1% (10 ppm benzene)

Figure 3



DETECTABLE COMPOUNDS

These include virtually all gases and vapors whose ionization potential is below 10.6 eV. Such a range encompasses a very large number of solvent materials and some important pollutant species including benzene, vinyl chloride, hydrogen sulfide, ethylene oxide, arsine and phosphine.

Figure 4

Compound	Relative Response
Acetone	0.452
Benzene	1.000
n-Butyl Acrylate	0.280
Diethylamine	0.509
Ethylene	0.043
Ethylene Oxide	0.130
Furfural	0.240
n-Hexane	0.085
n-Heptane	0.147
Iso-butylene	0.589
Iso-propyl Alcohol	0.046
Methyl Ethyl Ketone	0.099
Propylene	0.454
Propylene Oxide	0.060
Toluene	0.814
1,1,1-Trichloroethane	0.010
1,1,2-Trichloroethylene	0.734
m-Xylene	0.900

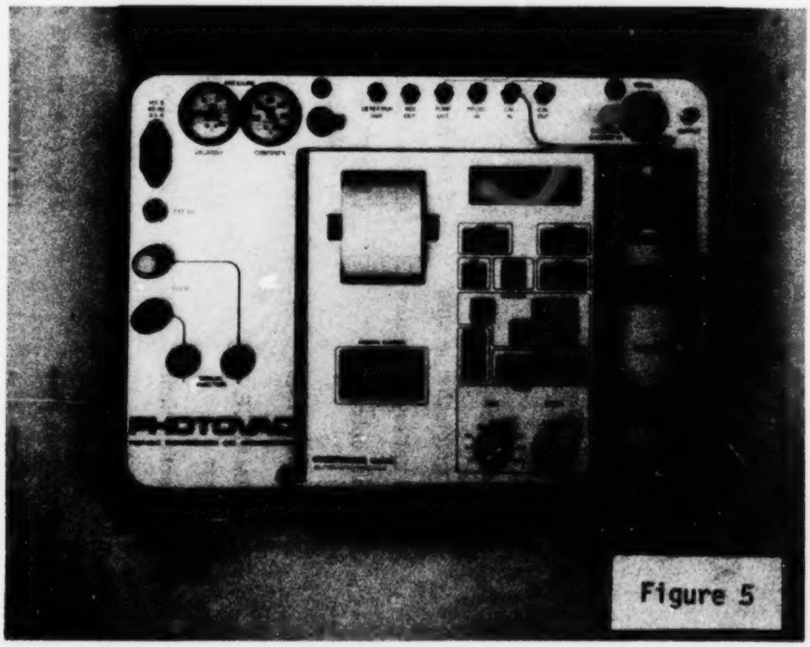


Figure 5

CHROMATOGRAM OF METHYLENE CHLORIDE, N-HEXANE AND BENZENE EACH AT APPROXIMATELY 10 PPM IN CLEAN AIR

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PHOTOVAC

1   COMPOUND        ID #  R.T.     LIMIT

METHYLENE CL        1    85.5 50.00 PPM
N-HEXANE            2   180.5 50.00 PPM
BENZENE             3   283.1 10.00 PPM
```

COMPOUNDS LISTED IN LIBRARY FILE #1

Figure 7

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PHOTOVAC
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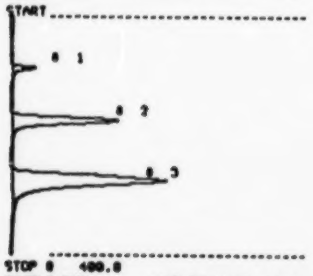

CHROMATOGRAM

```
STOP #   400.0
SAMPLE RUN          AUG 28 1985  11:39
ANALYSIS #     2    CENTRONICS LTD.
TEMPERATURE   27    ANALYT-PRE.SE-30
GAIN           2    F1 15mL F2 15mL

OFFSET              0.0 mV
CHART SPEED         0.5 cM/Min
SLOPE SENS.        10   mV/Sec
WINDOW     +/-     10   Sec
MINIMUM AREA        5   mVSec
PLOTTER DELAY      10.0 Sec
ANALYSIS TIME     400.0 Sec
CYCLE TIME          0   Min

COMPOUND NAME   PEAK  R.T.   AREA/PPM

METHYLENE CL      1    88.5 10.50 PPM
N-HEXANE          2   178.5 10.32 PPM
BENZENE           3   280.7 10.42 PPM
```

Time of Analysis

SUMMARY OF ANALYSIS PARAMETERS

RETENTION TIMES AND CONCENTRATIONS OF COMPOUNDS IDENTIFIED FROM LIBRARY FILE

```
PHOTOVAC

AUG 28 1985   11:39

SOURCE FIELD:  28
SOURCE POWER:  41

SAMPLE    LEVEL     0.0     10.0
CAL       LEVEL     0.0      5.0
EVENT 3   LEVEL    10.0     70.0
EVENT 4   LEVEL    10.0     10.5
EVENT 5   LEVEL    10.5     70.0
```

PROGRAM OF SAMPLING AND PRECOLUMN/BACKFLUSH ANALYSIS

Sampling time
Calibrant sample time
Analysis flow period through sample loop and precolumn
Injection time
Analysis flow period through precolumn

F_1 = Analytical Flow Rate
F_2 = Backflush Flow Rate

MODELLING OF THE SHORT TERM BEHAVIOUR OF PCB SPILLS

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Toronto and Kitchener, Ontario

and

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ABSTRACT

Work on a Technical Information for Problem Spills (TIPS) manual for polychlorinated biphenyls (PCBs) is currently underway. This paper outlines the approach to evaluating PCB spills that will be used in the PCB EnviroTIPS manual, and highlights portions of the work for which significant progress has been made to date. In particular, the aspects of the PCB EnviroTIPS manual that are specific to PCBs or represent modifications or improvements to the previous EnviroTIPS methodology are discussed. Specific discussions include: the types and relative volumes of PCB fluids in existence, the containers typically used to house these PCB fluids and the nature of the PCB spills that have occurred in the past; the procedures developed for estimating physical-chemical properties for the various PCB fluids from the available data base; and the methodology proposed for evaluating the short term behaviour of PCB spills in soils.

INTRODUCTION

The Technical Information for Problem Spills (TIPS) manuals were initiated by the Environmental Emergency Branch, Environment Canada in 1981 to provide a single source of comprehensive information on chemicals which are spilled frequently in Canada. The manuals were intended to be used by spill specialists for contingency planning and for designing countermeasures for spills. The manuals provide a wide range of data including contaminant properties, environmental behaviour, health effects, aquatic toxicology and countermeasures.

To date the EnviroTIPS series has focussed on commercial chemicals currently being manufactured. However, due to recent celebrated cases such as the Kenora, Ontario spill it was decided to prepare a manual dealing with PCBs and PCB-containing fluids.

This paper presents an overview of the approach to assessing the short term environmental behaviour of PCB spills that will be used in the PCB EnviroTIPS manual. Selected aspects of the work for which significant progress has been made to date are discussed in additional detail.

OVERVIEW

The behaviour of spilled PCB fluid after a spill event can be subdivided into short term and long term behaviour. For the purposes of this work, the time period over which the short term spill behaviour occurs is defined as being within hours or days of the spill event. The assessment of short term spill behaviour is therefore an important component of the EnviroTIPS program, as it is required in support of emergency response decisions. Long term behaviour of spilled PCB material is defined to occur over periods of months and years. For this time period, the PCB EnviroTIPS manual will be orientated toward understanding PCB fluid transport and fate with regard to the impacts of these phenomena on cleanup requirements. Long term spill behaviour will be addressed in detail in the PCB EnviroTIPS manual; however, it will not be specifically discussed in this paper.

Tools will be included in the PCB EnviroTIPS manual to permit the evaluation of the short term behaviour of PCB spills in the atmosphere, in bodies of water and below ground surface. An integral part of the assessment of short term behaviour is the evaluation of the exposure of humans and other life forms to the PCB spill event. The intent for the PCB EnviroTIPS manual is to relate the environmental PCB concentrations estimated through modelling to exposure. In particular, the incremental exposure resulting from a PCB spill event is of interest. While the evaluation tools for the short term behaviour of PCB spills may include sophisticated models with extensive data requirements, the orientation in the EnviroTIPS manual will be to provide the information in a simplified form, with a particular emphasis on nomographs, for use by the non-specialist.

The basic format of the PCB EnviroTIPS manual is anticipated to be the same as this paper, which is as follows:

- PCB fluid types
- PCB container types and reported spill scenarios
- Estimated physical-chemical PCB fluid properties
- Transport of spilled PCBs
- Exposure analysis

The behaviour of a PCB spill is highly dependent on the type of PCB fluid spilled, the type of container from which the spill occurred and the nature of the spill (e.g. due to gravity leakage as opposed to overpressurization and explosion). Because of the large variety of PCB and PCB-contaminated fluids that are in existence and types of containers used to house these fluids, the most common mixtures and container types must first be identified. These mixture and container types, along with reported PCB spill instances, can then be used to select relevant spill scenarios for inclusion in the PCB EnviroTIPS manual.

Estimates of the physical-chemical properties for the selected PCB mixtures are required for input to the spill behaviour models, which consist of environmental transport and exposure models. The transport and exposure models are developed based on the spill scenarios selected for evaluation, for use by spill personnel assessing health hazards and making emergency response decisions for actual spill events.

Pharmacokinetic models represent the next step in the above list of evaluations and analyses, in that they relate exposure to tissue concentrations. Efforts are currently underway to prepare such models to more specifically evaluate the impacts of PCB spill events on human health.

PCB FLUID TYPES

Polychlorinated biphenyls (PCBs) is a generic name for a large number of synthetic organic compounds comprised of a mixture of different chlorinated biphenyl isomers. Theoretically, 210 chlorinated biphenyls can exist including one non-chlorinated isomer, but only half that number are typically found due to steric hindrances.

The properties that have made PCBs useful commercially include thermal and chemical stability, and high dielectric properties. The main use of PCBs have been in electrical components such as transformers and capacitors, and also in cutting oils and other specialized lubricants. PCBs have low solubility in water (i.e. are highly lipophilic), low vapour pressures, and are relatively dense. They are relatively resistant to biodegradation, typically exhibiting half-lives of 8-15 years in environmental systems. The higher chlorinated isomers are in general, more persistent than the lower chlorinated congeners.

In North America, PCBs were manufactured between 1929 to 1977 by the Monsanto Company and its predecessors. Although they have been distributed under a wide number of trade names, the Monsanto commercial mixtures, known as Aroclors, are the most prevalent. PCBs used in Canada have been predominantly imported from the United States. Since 1980, the use of PCBs in Canada has been restricted to closed electrical equipment such as transformers; however, use of the substance as a dielectric/heat transfer medium is being phased out.

Due to the large variety of PCB and PCB-contaminated fluids that are in existence, the most common PCB mixtures were first identified. In this way efforts to determine physical-chemical properties and relevant spill scenarios could be performed for these selected PCB mixtures.

A review of national and provincial PCB inventories has shown that on a national scale, 87 percent (Environment Canada, 1985) of the total volume of PCB fluids are in use in electrical applications, whereas in Ontario (Ontario Ministry of the Environment, 1984), usage in electrical applications accounts for 99 percent of the provincial inventory. The generic name for PCB fluids and other nonflammable synthetic chlorinated aromatic hydrocarbons used as electrical insulating media is Askarel. The PCB fluids used in this fashion can be generally categorized as either transformer (65 percent of all electrical applications) or capacitor (35 percent of all electrical applications) Askarels.

Capacitor Askarels generally consist entirely of PCB fluids. The historical trends in the manufacture and use of PCBs as capacitor Askarels are as follows (Lawton et al, 1985):

Time Period	PCB Fluid Type
Pre 1953-55	Aroclor 1254
1955 - 1971	Aroclor 1242
1971 - 1977	Aroclor 1016

Standard specifications for these Askarels are provided by the American Society for Testing and Materials (ASTM, 1983a).

The ASTM specifications for transformer Askarels (ASTM, 1983b) list seven Askarels containing 45 percent or more PCB fluids by weight. The dominant commercial transformer Askarels used in Canada are Aroclor 1254-trichlorobenzene mixtures. Inerteen, which was manufactured by Westinghouse, contains 70 percent Aroclor 1254 and 30 percent trichlorobenzene, and Pyranol, which was manufactured by General Electric, contains 60 percent Aroclor 1254 and 40 percent trichlorobenzene. Other Aroclors have been used in other types of electrical devices. For example, Aroclor 1248 is employed in compensators.

A variety of other materials, including oils, solvents and solid wastes, are known to be contaminated with PCB fluids. Mineral oils have been identified as a material type of which large quantities have been contaminated with PCBs. Generally, the PCB contamination of mineral oils ranges from 50 to 50,000 ppm (Edison Electric Institute, 1982) and thus the mineral oil physical-chemical properties are applicable for these fluids. The total volume of contaminated mineral oils in Canada is unknown.

PCB CONTAINER TYPES AND REPORTED SPILL SCENARIOS

In addition to identifying common PCB fluid types, it is also important to identify the container types commonly used to house PCB fluids. The container types along with their volume capacities aid in evaluating the nature and magnitude of potential spill events. Common container types and container volumes are as follows:

Container Type	Container Volume	PCB Fluid Type
Capacitors	20 mL - 25 L	Askarel
Transformers	180 L - 45,000 L	Askarel/Oil
Drums	200 L	Askarel/Oil
Tank Trucks	45,000 L	Oil

The use of drum and tank truck containers is limited to the storage and transport of PCB fluids, and capacitors and transformers house the bulk of the existing PCB inventories in Canada. It is therefore not suprising that the most frequently reported type of PCB spill in British Columbia is due to capacitor leakage (Garrett, 1983).

Based on a preliminary review of the available data, the majority of PCB spills in Canada result in less than 50 litres of spilled fluid.

Leakage is generally due to gravity flow from a faulty seam or crack; however, PCB fluids are occasionally spilled due to the overpressurization of a transformer. While fires are rarely caused by PCB spills, there is a large spread hazard potential in the event that a fire does result in a PCB spill area.

ESTIMATED PHYSICAL-CHEMICAL PCB FLUID PROPERTIES

The physical-chemical properties of the PCB fluids of interest represent important inputs to the spill behaviour models. The accurate definition of these properties is particularly difficult, however, for two reasons. The first is the large number of PCB congeners that may be present in a PCB fluid. PCB fluids are often mixed with trichlorobenzene (transformer Askarels) and mineral oils (insulating oils), in addition to other fluids. Thus there are a multiplicity of possible PCB mixtures. The second difficulty in accurately defining the properties of PCB fluids is the lack of available data. The physical-chemical property data for PCBs are fragmented, with few properties defined for many congeners, and little to no definition of the variations of these properties with temperature.

The basic assumption that has been made in the physical-chemical property estimation procedures is that the properties are equal for PCB congeners with the same number of chlorine atoms (or chlorine number). This reduces the number of "pure" PCB fluid types requiring physical-chemical property definition to eleven: biphenyl,monochlorobiphenyl, dichlorobiphenyl, trichlorobiphenyl, tetrachlorobiphenyl, pentachlorobiphenyl, hexachlorobiphenyl, heptachlorobiphenyl, octachlorobiphenyl, nonachlorobiphenyl, and decachlorobiphenyl. The word "pure" is placed in quotations due to the fact that the locations of the chlorine atoms in the PCB congeners of equal chlorine number do affect the physical-chemical properties of the so called pure PCB fluid to varying degrees depending on the property of interest.

Using interpolative methods and the available physical-chemical data, mean values for the properties have been estimated for each of the eleven PCB fluid types at standard conditions. Appropriate temperature conversion factors can be used to modify these estimates for different temperatures. For example, published coefficients of volume expansion are used for temperature corrections for density, whereas enthalpy-type correction factors are used for vapour pressure and solubility.

The mixtures of PCB congeners in the various Aroclor types are defined, and therefore appropriate mixing rules can be used to estimate properties for the Aroclors of interest. This concept can be extended to PCB mixtures containing trichlorobenzene and/or mineral oils. A computer program has been developed for estimating PCB mixture properties from the estimated properties for the eleven "pure" PCB fluid types and other fluid types. Examples of mixing rules used include the Le Bas additive volumes method for density (Reid et al, 1977), and Raoult's Law for vapour pressure. Physical-chemical properties computed with this program for Askarels with known property values have been compared to those properties in order to validate the computer program, and appropriate modifications have been made to the "pure" substance properties, temperature conversion factors and mixing rules as required. This reconciliation of published data and computed properties has been made over a range of temperatures.

The net result is a computer program which can be used to generate tables, graphs and nomographs of physical-chemical property data for PCB mixtures. An example calculation is shown in Table 1 for Aroclor 1254 at standard conditions (25 C), and at 5 C using temperature conversion factors. It is believed that this approach may be a useful prototype for treating other chemical mixtures.

Other properties such as flammability characteristics, decomposition products and thermodynamic properties will also be gathered in accordance with the general EnviroTIPS practice.

TRANSPORT OF SPILLED PCBs IN THE ENVIRONMENT

The extent and rates at which spilled PCBs move in the environment must be approximately known to confidently assess the resultant health hazards and to develop effective countermeasures. As shown in Figure 1, the transport of spilled PCBs through the atmosphere, with water bodies and bed sediments, and below ground surface will be addressed in the PCB EnviroTIPS manual to assist spill specialists in the assessment of the short term behaviour of spilled PCBs. Figure 1 also illustrates that exposure to humans and other life forms is the ultimate concern in all spill circumstances.

Transport in the Atmosphere

PCBs can move into the atmosphere above spill sites due to volatization. It is proposed to estimate evaporative loss to the atmosphere with the model of Kawamura and MacKay (1985). Transport through the atmosphere will be modelled with a standard Gaussian plume model for a ground-level area source. For a critical concentration C_0, nomographs based on this model will be provided for the estimation of the distance downwind at which C_0 occurs and the area and maximum width of the region enclosed by the C_0 isopleth. Because of the nature of the PCB source (ground-level spill), the time frame of interest (on the order of an hour or more) and the fact that estimates may be conservative, the analysis methodology accounts for only two of the six stability conditions: neutral (D class) for all daylight hours and windy nights and stable (F class) for nights with low wind speeds.

Transport in Water

Askarels are more dense than water and therefore will sink and interact with sediment. In contrast mineral oils are less dense and would be expected to float on water surfaces. Transport-in-water calculations and nomographs will therefore account for both phenomena. As well, efforts will be made to account for the interactions of spilled PCBs with bed sediments and their subsequent movement. Detailed procedures have as yet not been developed for this aspect of the short term modelling.

TABLE 1. ESTIMATED PHYSICAL-CHEMICAL PROPERTIES FOR AROCLOR 1254

COMPONENT	MASS FRACTION	MOLE FRACTION	VOLUME FRACTION
Biphenyl	- - -	- - -	- - -
Monochorobiphenyl	- - -	- - -	- - -
Dichlorobiphenyl	0.005	0.007	0.006
Trichlorobiphenyl	0.010	0.013	0.011
Tetrachlorobiphenyl	0.210	0.235	0.222
Pentachlorobiphenyl	0.485	0.486	0.486
Hexachlorobiphenyl	0.230	0.209	0.220
Heptachlorobiphenyl	0.060	0.050	0.055
Octachlorobiphenyl	- - -	- - -	- - -
Nonachlorobiphenyl	- - -	- - -	- - -
Decachlorobiphenyl	- - -	- - -	- - -
Mineral Oil	- - -	- - -	- - -
Trichlorobenzene	- - -	- - -	- - -
TOTAL	1.000	1.000	1.000

MIXTURE PROPERTIES AT 25 DEG C

Mean Molecular Mass	3.27×10^{2} g/mol
Molecular Volume	2.12×10^{2} cm^{3}/mol
Density	1.55×10^{3} kg/m^{3}
Vapour Pressure	1.16×10^{-2} Pa
Water Solubility of Liquid	4.64×10^{-4} mol/m^{3}
Water Solubility of Liquid	1.37×10^{-1} g/m^{3}
Viscosity	2.28×10^{3} mPa·sec
Henry's Law Constant	2.51×10^{1} Pa·m^{3}/mol
Air/Water Partition Coefficient	1.08×10^{-2} dimensionless
Boiling Point	4.65×10^{2} deg C

DEDUCED PROPERTIES AT 5 DEG C

Molecular Volume	2.09×10^{2} cm^{3}/mol
Density	1.56×10^{3} kg/m^{3}
Vapour Pressure	1.69×10^{-3} Pa
Water Solubility of Liquid	3.47×10^{-4} g/m^{3}
Viscosity	1.33×10^{5} mPa·sec
Henry's Law Constant	4.87×10^{0} Pa·m^{3}/mol
Air/Water Partition Coefficient	2.11×10^{-3} dimensionless

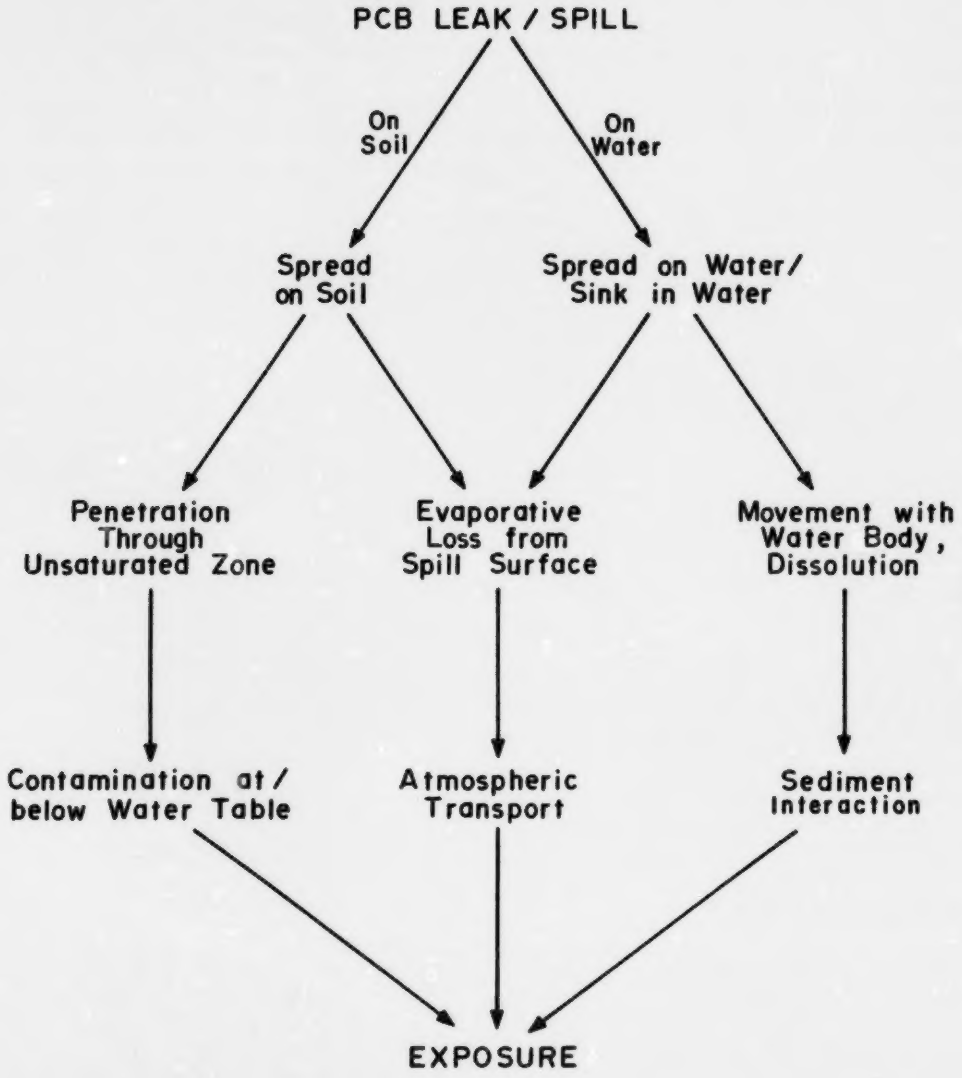

PCB LEAK / SPILL
On Soil
On Water
Spread on Soil
Spread on Water/ Sink in Water
Penetration Through Unsaturated Zone
Evaporative Loss from Spill Surface
Movement with Water Body, Dissolution
Contamination at/ below Water Table
Atmospheric Transport
Sediment Interaction
EXPOSURE

FIGURE 1. TRANSPORT MECHANISMS FOR SPILLED PCB FLUIDS

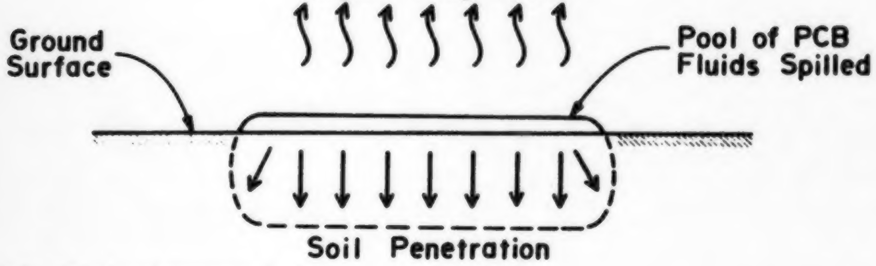
Transport in Soils

In previous EnviroTIPS manuals, the evaluation of the transport of spilled materials through soil has been limited to that in the unsaturated zone. The transport of PCBs at or below the water table is in fact the most serious problem with regard to the subsurface transport of PCBs, or any contaminant, due to the importance of groundwater as a drinking water source in many areas. As such, information and nomographs for the assessment of PCB transport at and below the water table will be included in the PCB EnviroTIPS manual. Because of this and several other improvements and modifications planned for the subsurface transport section of the PCB EnviroTIPS manual, this section of the manual is described in more detail below.

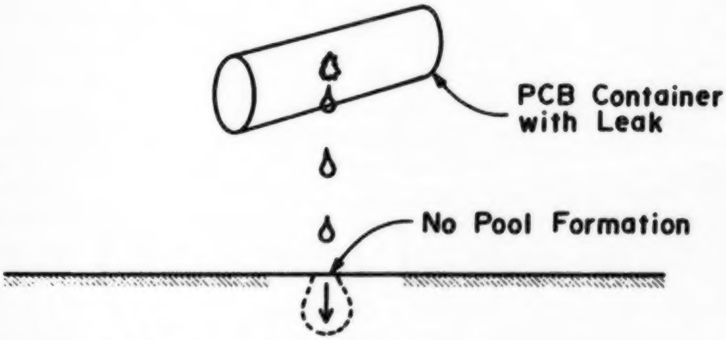
SUBSURFACE TRANSPORT OF SPILLED PCBs

As shown in Figure 1, the first task in assessing a PCB spill on land is to understand the nature of the spill event and the formation of the spill pool. Figure 2 shows three spill scenarios which are currently being evaluated for the PCB EnviroTIPS manual. Figure 2a depicts a spill event where a fixed volume of PCB fluid is spilled onto the ground over a time period that is short in comparison to the times required for significant soil penetration and evaporation to occur. Soil penetration and evaporation then occur in essentially uniform fashions from the pool of spilled PCB fluids. Raisbeck and Mohtadi (1974) provide equations to estimate pool size that are applicable to the spill scenarios in Figures 2a and 2c. Figures 2b and 2c depict spill events that occur over longer periods of time. In Figure 2b, the PCB leak rate per unit area of the spill area is less than the transmissive capacity (Darcy flux for saturated conditions) of the soil, and consequently a pool of spilled PCBs is not formed. Figure 2c shows a spill event where the PCB leak rate per unit area of the spill pool is greater than the transmissive capacity of the soil. In these instances, a pool of PCBs forms and the pool size increases until the leaking PCBs are distributed over an area such that the PCB leak rate (L^3/T) divided by the pool area (L^2) is equal to the transmissive capacity of the soil (L/T). As illustrated in Figure 2c, the depth of penetration is greatest directly beneath the container leak for this spill scenario.

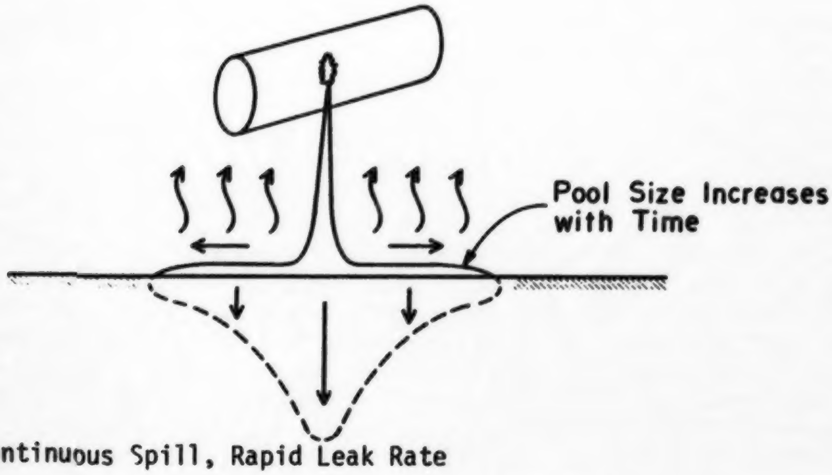
The approach to assessing the subsurface transport of spilled PCB fluids is illustrated in the following paragraphs for the spill scenario shown in Figure 2a. The PCB fluids of interest are relatively insoluble in water, and consequently, when spilled onto soil, the infiltration and transport downward through the soil involve multi-phase phenomena. The phases of concern are the PCB fluid, water, soil and the soil gases. Due to the complexities of these multi-phase phenomena and the limited information available on the movement of PCB fluids through soil, simplifications in the representations of soil and groundwater conditions are required. The subsurface movement of immiscible oils have been more extensively studied (e.g. Schwille, 1967; Van Dam, 1967), and the principles observed are applied, by analogy, to the subsurface movement of PCB fluids.


Slight Evaporation
Ground Surface
Pool of PCB Fluids Spilled
Soil Penetration

(a) Instantaneous Spill


PCB Container with Leak
No Pool Formation

(b) Continuous Spill, Slow Leak Rate


Pool Size Increases with Time

(c) Continuous Spill, Rapid Leak Rate

FIGURE 2. PCB SPILL SCENARIOS ON SOIL

The subsurface movement of PCB fluids is assumed to occur as shown in Figure 3. It is assumed that when the spill occurs, the soil contains water only up to its field capacity and that this condition prevails down to the groundwater table. The spilled PCB liquid fills the pores at the soil surface and begins to penetrate downward. It is assumed that the PCB fluid moves downward through the soil according to Darcy's Law as a saturated slug, but leaving behind a constant residual amount within the soil pores.

Downward tranport continues until the volume of PCB fluid spilled per unit area, or the initial pool thickness, equals the amount retained in the soil as residual PCB fluid. Some lateral spreading may occur due to capillary action. If the initial pool thickness requires a depth of unsaturated soil greater than the depth to the water table to exhaust the resultant saturated slug of PCB fluid as residual PCB fluid, then the PCB fluid will reach the water table. PCB fluids that are less dense than water, such as mineral oils contaminated with PCBs, will spread within the capillary fringe in the shape of a pancake, as shown in Figure 3. PCB fluids that are more dense than water, such as Askarels, will tend to sink below the water table and continue to migrate in a downward direction.

A flowchart is provided in Figure 4 that outlines the basic steps for evaluating subsurface transport for the spill scenario shown in Figure 2a. After assessing the thickness and areal extent of the pool of spilled PCBs, vertical penetration through the unsaturated zone is evaluated. A nomograph will be provided to predict the ultimate vertical penetration distance as a function of soil type and the initial thickness of the pool of spilled PCB fluids. Residual oil saturation has been shown to be a function of soil type (Schwille, 1975; Dietz, 1971), and thus the depth of soil required to exhaust a given initial spill thickness, which is called the ultimate vertical penetration distance, can be calculated as a function of soil type.

A second nomograph will be provided showing the relationship between penetration depth and penetration time as a function of soil type and PCB fluid type. This nomograph will permit the estimation of ultimate penetration time, and the times at which intermediate depths of penetration occur.

As the PCB fluids infiltrate into the soil, there is a concomitant reduction in the pool thickness of the PCB spill. This information is required for the evaporation model described in the previous section.

For instances where the predicted ultimate depth of penetration is greater than the known water table depth, the calculations continue to assess the more serious problem of PCB contamination at/below the water table. The time of penetration to the water table is calculated using the depth-time nomograph described above.

The work of Schwille (1967) and Dietz (1971) with oils shows that the pancake-shaped lense of fluid formed by fluids that are less dense than water occurs in the zone of water saturation ranging from 75 percent to 85 percent. The thickness of this zone can be related to soil type. Thus a nomograph will be provided to estimate the areal extent of the "pancake" of residual PCB saturation for the volume of PCB fluid reaching the water table, as a function of soil type.

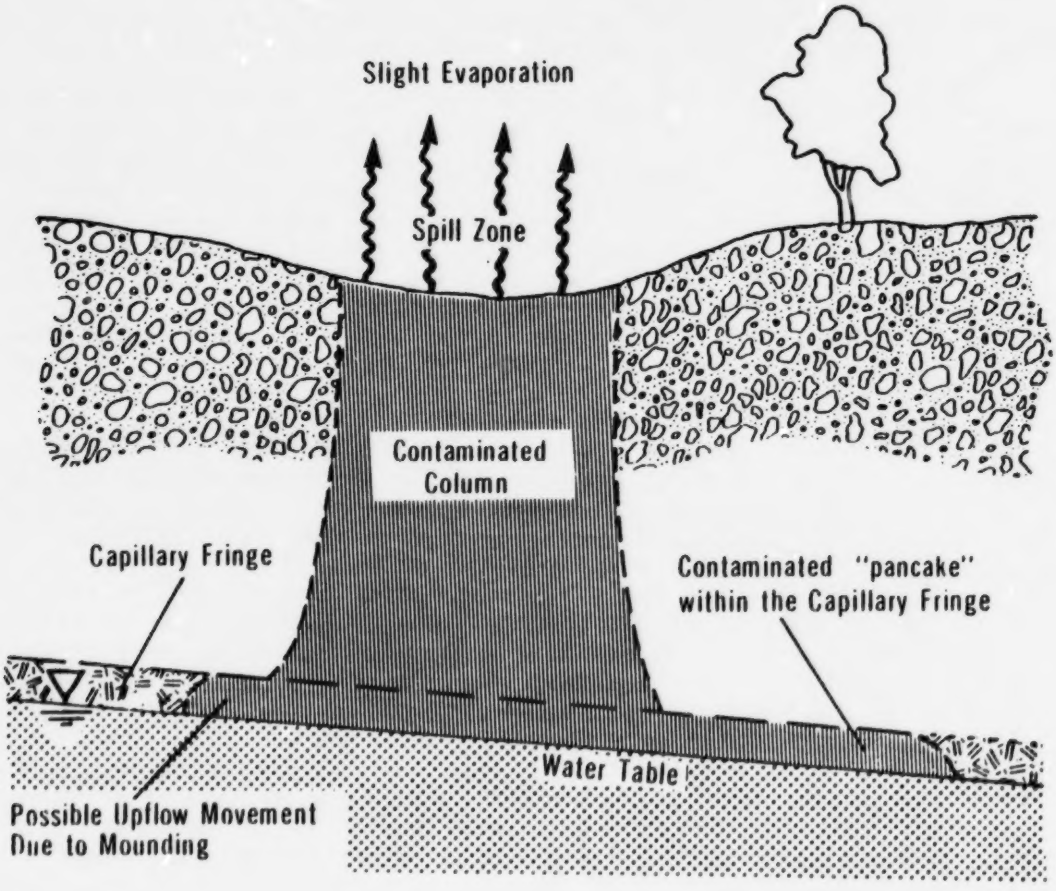

Slight Evaporation
Spill Zone
Contaminated Column
Capillary Fringe
Contaminated "pancake" within the Capillary Fringe
Water Table
Possible Upflow Movement Due to Mounding

FIGURE 3. SUBSURFACE TRANSPORT OF PCB FLUIDS LESS DENSE THAN WATER

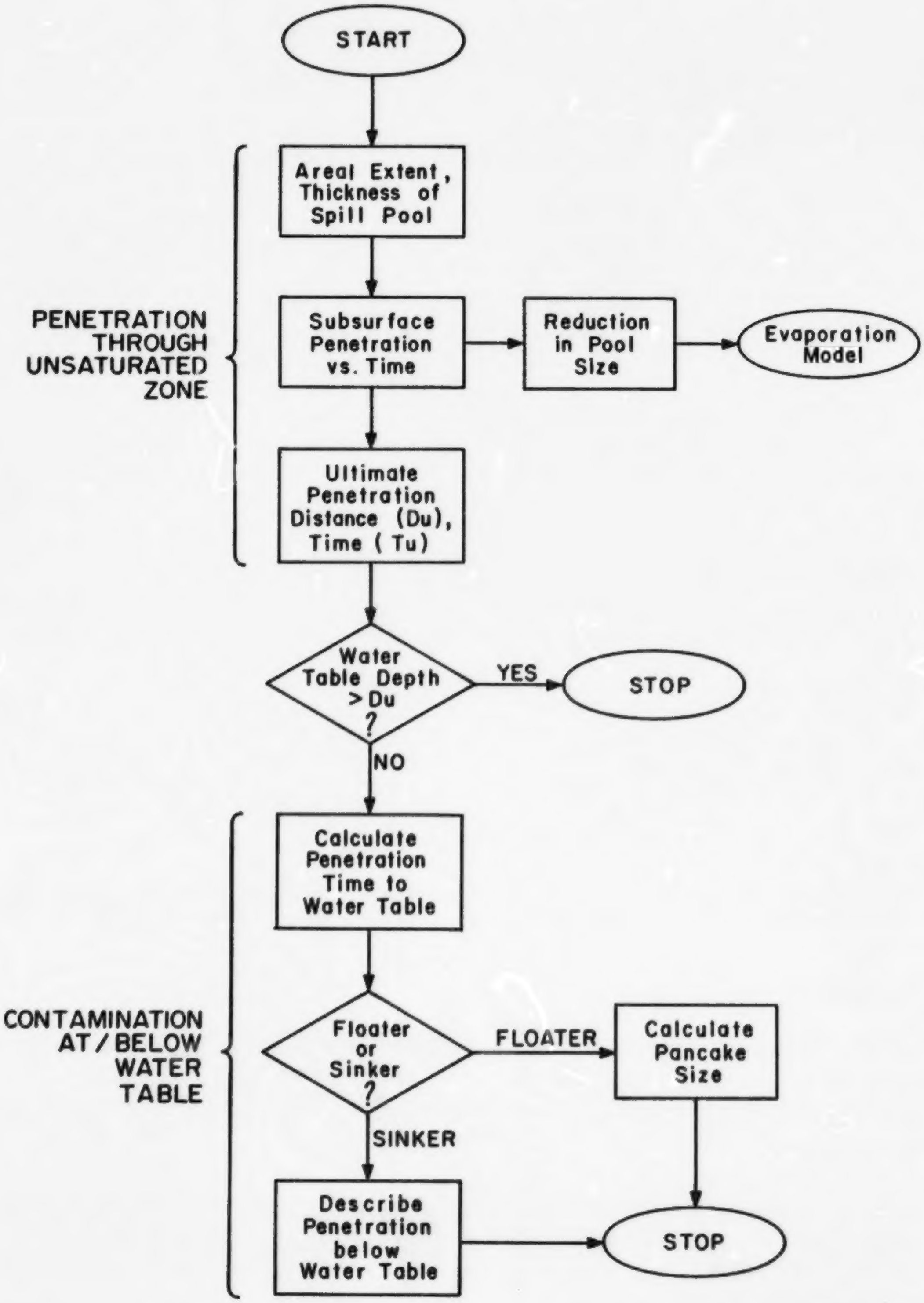

START
Areal Extent, Thickness of Spill Pool
PENETRATION THROUGH UNSATURATED ZONE
Subsurface Penetration vs. Time
Reduction in Pool Size
Evaporation Model
Ultimate Penetration Distance (Du), Time (Tu)
Water Table Depth > Du ?
YES
STOP
NO
CONTAMINATION AT/BELOW WATER TABLE
Calculate Penetration Time to Water Table
Floater or Sinker ?
FLOATER
Calculate Pancake Size
SINKER
Describe Penetration below Water Table
STOP

FIGURE 4. FLOWCHART FOR ASSESSING SUBSURFACE PCB TRANSPORT

PCB fluids that sink below the water table are not expected to be significantly influenced by the horizontal movement of the groundwater, as the downward density gradient is expected to be much larger than any horizontal, water table gradients. The PCB fluids will move at a rate below the water table that is less than that in the unsaturated zone, as water is significantly more dense and viscous than the soil gases.

EXPOSURE ANALYSIS

Canadians are routinely exposed to PCBs resulting from trace quantities found in the air, foods and drinking water. It has been estimated (CANVIRO, 1985) that the average Ontarian who does not eat freshwater fish has a "typical" intake of 9µ g/d of PCBs from all exposure routes.

In assessing the significance of a PCB spill, one measure that can be used is the estimated additional or incremental human intake resulting from the spill. Through pharmacokinetic modelling this incremental intake can be translated into the increase in tissue burden.

The PCB EnviroTIPS manual will at a minimum incorporate procedures for estimating incremental exposure. The pharmacokinetic modelling is advancing; however, it is not certain at this time whether the output of the model will be available for incorporation into the manual.

SUMMARY

To date, much has been learned about the types and relative volumes of PCB fluids in existence, the containers typically used to house these PCB fluids and the nature of PCB spills that have occurred in the past. An innovative approach is being developed to estimate relevant physical--chemical properties for PCB fluids from the limited available data base. Based on the previous PCB spill experiences and the knowledge gained about the common PCB fluid and container types, transport and exposure models are being developed to describe the behaviour of PCB spills. In many cases these models represent improvements to the previous EnviroTIPS methodology, or PCB-specific modifications to that methodology to better evaluate PCB spills. Finally, work is underway to develop pharmacokinetic models to relate PCB spill exposure to tissue concentrations, to better evaluate the health effects of PCB spill events.

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DEUX SYSTEMES INFORMATISES POUR LA PREVISION DU COMPORTEMENT DES POLLUTIONS EN MILIEU MARIN

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RESUME

La présente communication décrit deux systèmes informatisés pour la prévision du comportement des pollutions en mer.

Pour le premier, il s'agit d'un système de programmes, accessible aux non-informaticiens, destiné à prédire l'évolution d'une pollution par hydrocarbures. Pour le réaliser, on a couplé interactivement trois modèles prédisant, d'abord, l'évolution des hydrocarbures en surface, ensuite, l'advection-diffusion de la phase dispersée, enfin, l'impact immédiat sur les ressources vivantes de la mer. Ce système est opérationnel depuis octobre 1985.

Le deuxième système est actuellement en cours de réalisation. Il décrira l'évolution des substances chimiques susceptibles de s'évaporer. Pour ce faire, on couplera deux modèles principaux : l'un pour prévoir le comportement de la nappe de polluant à la surface de la mer, l'autre pour prévoir l'évolution du nuage gazeux. Ces modèles seront couplés interactivement et l'impact d'un éventuel nuage toxique sera aussi envisagé.

INTRODUCTION

L'Unité de Gestion des Modèles Mathématiques de la Mer du Nord et de l'Estuaire de l'Escaut (UGMM) est un organisme gouvernemental belge, créé il y a une dizaine d'années pour assurer la coordination de la recherche océanographique et pour exécuter des études relatives au milieu marin. Ses activités sont nombreuses et variées : surveillance de la qualité des eaux côtières, mesures courantométriques, analyse de données, organe de contact pour les problèmes de pollution, exécution d'études d'impact pour le gouvernement ou pour des tiers, élaboration et exploitation de modèles mathématiques,...

C'est dans ce cadre que l'UGMM a été chargée par la Commission des Communautés Européennes (Direction Générale de l'environnement, de la protection des consommateurs et de la sécurité nucléaire) de réaliser deux systèmes informatisés opérationnels répondant aux questions suivantes :

- soit un polluant qui flotte à la surface de la mer et dont une fraction importante pénètre dans la colonne d'eau. Quelle est l'évolution de la pollution en surface ? Quelle est l'évolution de la pollution dans la colonne d'eau ? Quel est l'impact de cette pollution sur le zooplancton ?
- soit un polluant qui flotte à la surface de la mer et dont une fraction importante s'évapore dans l'atmosphère. Quelle est l'évolution de la pollution en surface ? Quelle est l'évolution de la pollution dans l'atmosphère ? Quelles sont les distances de sécurité à respecter autour du lieu de l'accident ?

Le premier de ces systèmes vise avant tout les pollutions par hydrocarbures mais la philosophie qui a présidé à sa réalisation permettra de prendre en compte tout produit chimique se comportant de manière semblable.

En outre, ces deux systèmes devaient être interactifs et utilisables par les spécialistes des pollutions en mer, qu'ils aient des notions d'informatique ou non. Ces systèmes devaient apporter des réponses dans deux situations bien définies : d'une part, en temps réel, en fournissant des prévisions aux équipes opérationnelles pour les aider à planifier les opérations de lutte, et d'autre part, en mode prospectif, pour servir de base à des études d'impact ou à l'entraînement des équipes du terrain.

Le premier de ces systèmes est réalisé et a déjà servi à des études d'impact. Le deuxième en est au début de sa réalisation et sera terminé pour l'automne 1986.

PRINCIPES

Pour que les systèmes, une fois réalisés, répondent effectivement aux besoins et soient réellement utilisables par le plus grand nombre, les aspects suivants ont été particulièrement étudiés :

Conception modulaire

Les différents modèles à prendre en considération pour chacun des systèmes sont mathématiquement très complexes et comprennent un grand nombre de variables et de paramètres. Les programmes qui y correspondent exigent donc beaucoup de ressources (ils "tournent" sur un ordinateur IBM 4341). Il était donc utopique d'envisager de construire un "super-modèle", c'est-à-dire un programme unique rassemblant tous les modèles nécessaires. La conception modulaire s'imposait donc, celle-ci permettant de plus une mise à jour beaucoup plus aisée du système.

Convivialité

Un des buts de ces projets est de donner aux spécialistes de la pollution en mer l'accès à des moyens puissants de simulation. Il est bien connu, en effet, que plus un programme est complexe, moins il y a de personnes qui peuvent l'utiliser. C'est pourquoi, comme les modèles envisagés étaient assez sophistiqués, un effort tout particulier a été fait pour les rendre accessibles. Ceci a porté sur :

- la gestion automatique des fichiers : le système gère la dénomination des fichiers, vérifie leur existence, impose leur création quand c'est nécessaire, et assure les liens avec les différents programmes.
- la clarté du dialogue : les systèmes devant être interactifs, les questions posées à l'utilisateur ont été rédigées de manière à éviter toute équivoque. Les réponses à entrer sont la plupart du temps présentées sous forme de menu. Lorsqu'il faut donner une valeur numérique, une valeur par défaut est proposée.
- le droit à l'erreur : un test de vraisemblance est effectué sur les valeurs entrées par l'utilisateur et s'il est négatif, la question est reposée.
- la lisibilité des résultats : la sortie traditionnelle des résultats (impression) permet d'accéder à une information très détaillée. Elle est néanmoins difficile à déchiffrer et donne rarement la possibilité d'avoir une vue d'ensemble de l'évolution d'une situation. C'est pourquoi un effort particulier a été fait pour traduire l'information sous forme de graphiques ou de cartes. Ces dessins sont disponibles à l'écran ou sur papier.

LE SYSTEME "OPIA" (Oil Pollution Impact Assessment)

Le système prenant en compte les pollutions qui se présentent sous la forme d'une nappe de surface se dispersant dans la colonne d'eau est devenu opérationnel durant l'automne 1985. Il s'agit d'une version restreinte puisque, comme son nom l'indique, seules les pollutions par hydrocarbures sont envisagées.

Pour utiliser ce système, il faut passer par trois phases distinctes :

i) Initialisation du système, identification de l'utilisateur et de l'application,

ii) Description des données environnementales (vents, vagues, courants),

iii) Simulation de la pollution, en surface puis dans la colonne d'eau et évaluation de l'impact sur les populations de plancton.

Les données concernant les vents et les vagues sont fournies par l'utilisateur quand il s'agit d'effectuer des études d'impact. Dans le cas de simulations en temps réel, on peut utiliser les prévisions fournies par télex par le "British Meteorological Office" (Bracknell, UK). Pour les courants, l'intention première était d'utiliser directement un des modèles hydrodynamiques que l'UGMM possède. Parmi ceux-ci, le modèle utilisé pour prédire les marées et les tempêtes en mer du Nord et dans la Manche semblait bien adapté. Il s'agit d'un modèle 2D (horizontal) aux différences finies calculant les courants et les élévations de la surface de la mer sous l'influence de la marée et des conditions météorologiques. Après quelques essais, il s'est avéré que l'usage direct du modèle entraînerait des coûts prohibitifs et, surtout, des délais incompatibles avec la notion de simulation en temps réel. La solution adoptée pour contourner cette difficulté est la suivante : les champs de courants induits par les principales composantes de la marée ont été calculés séparément par le modèle et ce, une fois pour toutes. Ensuite, en fonction de l'instant choisi par l'utilisateur pour le début de la simulation, un programme effectue la recomposition harmonique des courants, autant de fois que nécessaire pour couvrir la durée de la simulation (typiquement 15 jours).

La simulation de la pollution en surface s'effectue actuellement par le modèle MU-SLICK, qui ne traite que les hydrocarbures. A l'avenir, celui-ci pourrait être remplacé par un modèle plus général, pour autant qu'il prédise aussi la quantité de polluant qui entre dans la colonne d'eau.

MU-SLICK a été développé par l'UGMM en vue d'effectuer tant des études prospectives que des simulations en temps réel lors d'accidents. Le modèle prend en compte les phénomènes suivants :

- advection de la nappe sous l'effet combiné des courants et des vents,
- étalement de la nappe sous l'effet des forces de gravité, d'inertie, de tension superficielle et de viscosité,
- vieillissement par évaporation, dispersion naturelle ou chimique, dissolution, mise en aérosols, émulsion et récupération mécanique.

Ce modèle a pu être inclus tel quel dans OPIA.

Le modèle utilisé pour prédire le comportement de la phase dispersée dans la colonne d'eau s'appelle MU-DISPER. Il a également été développé par l'UGMM et il est régulièrement employé pour simuler les rejets - autorisés ou accidentels - de produits chimiques en mer. Ce modèle utilise une méthode sophistiquée de résolution de l'équation d'advection-diffusion où les problèmes numériques, inhérents au traitement de cette équation sur ordinateur, sont réduits au maximum. Il est conçu pour simuler jusqu'à dix variables d'état qui interagissent, ou pas, entre elles ou avec le milieu.

L'estimation de l'impact sur le zooplancton devait se faire au départ grâce à un modèle séparé. Il est apparu assez rapidement que la structure de MU-DISPER permettait une solution plus élégante. Pour ce faire, nous avons considéré trois variables d'état :

i) la concentration d'hydrocarbures dans la colonne d'eau,
ii) la densité de population du zooplancton perturbé par l'hydrocarbure et soumis comme lui à l'advection et à la diffusion,
iii) la densité de population du zooplancton telle qu'elle existerait sans l'influence de la pollution, c'est-à-dire affectée uniquement par les courants. La perturbation induite par la première variable sur la deuxième est estimée par une fonction-seuil. L'introduction de la troisième variable (la population de référence) permet d'exprimer l'impact très simplement pour les différences locales et instantanées entre la population perturbée et la population non-perturbée.

Application

Le système OPIA a été utilisé jusqu'à présent pour effectuer des études d'impact. Leur but était d'estimer l'effet négatif que l'usage de dispersants, nécessaire pour réduire la présence d'hydrocarbures sur les plages proches, pouvait avoir sur la population zooplanctonique. Chaque étude nécessitait donc deux simulations avec OPIA, l'une sans et l'autre avec l'effet de la dispersion chimique, toutes les autres conditions restant égales.

Un scénario type est le suivant :

- zone : baie sud de la mer du Nord.
- période : première quinzaine du mois d'avril. Il y correspond une présence importante d'oeufs de sole dans la zone précitée.
- hydrocarbure : 10 000 m^3 de brut du Kowait.
- moyens de lutte : aucun dans un cas. Dans l'autre, taux maximal déterminé par les moyens réellement disponibles dans cette zone.

Les figures 1 à 6 sont un échantillon des dessins produits par le système tout au long de la simulation.

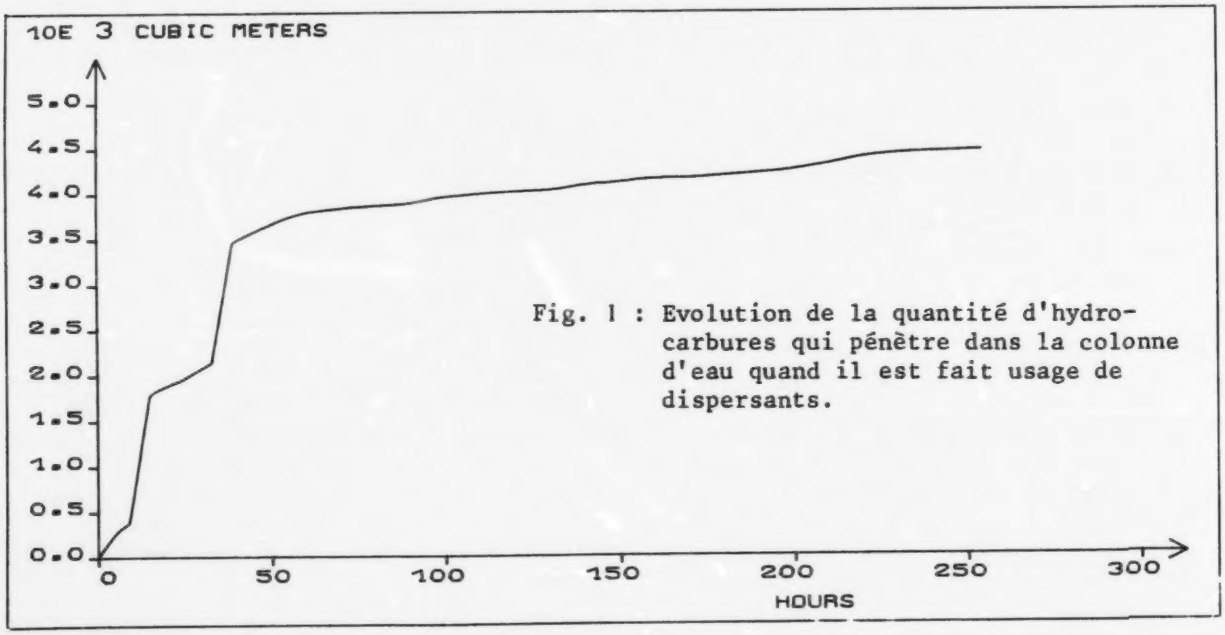

Fig. 1 : Evolution de la quantité d'hydrocarbures qui pénètre dans la colonne d'eau quand il est fait usage de dispersants.

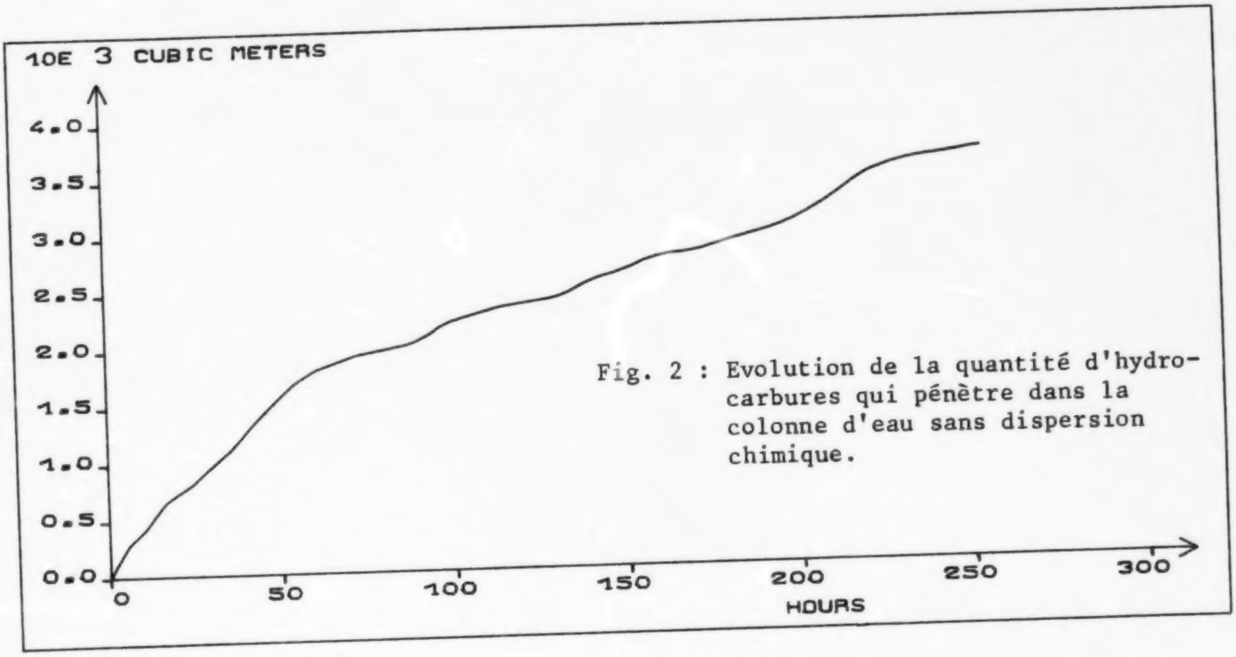

Fig. 2 : Evolution de la quantité d'hydrocarbures qui pénètre dans la colonne d'eau sans dispersion chimique.

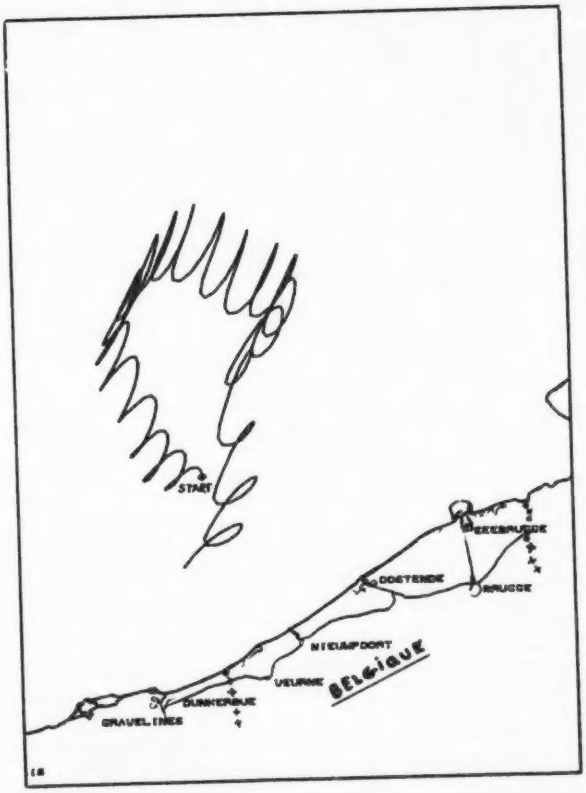
START
ZEEBRUGGE
OOSTENDE
BRUGGE
NIEUWPOORT
VEURNE
BELGIQUE
DUNKERQUE
GRAVELINES

Fig. 3 : Trajectoire complète de la pollution en surface.

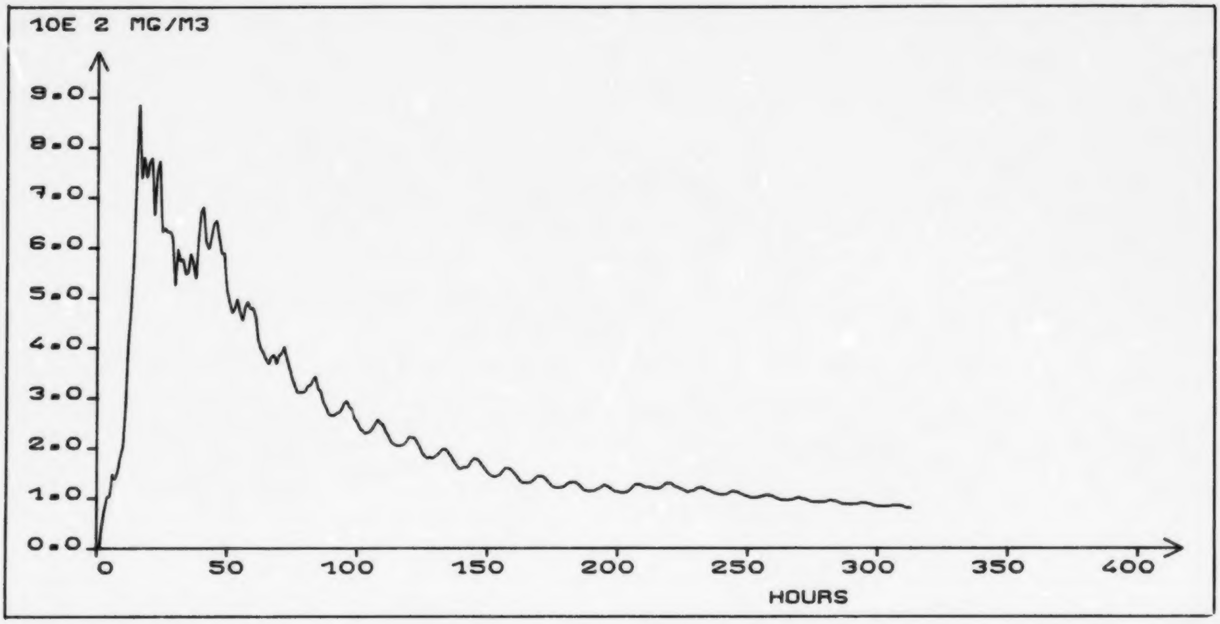

Fig. 4 : Evolution du maximum de concentration en hydrocarbures dans dans la colonne d'eau avec la dispersion chimique.

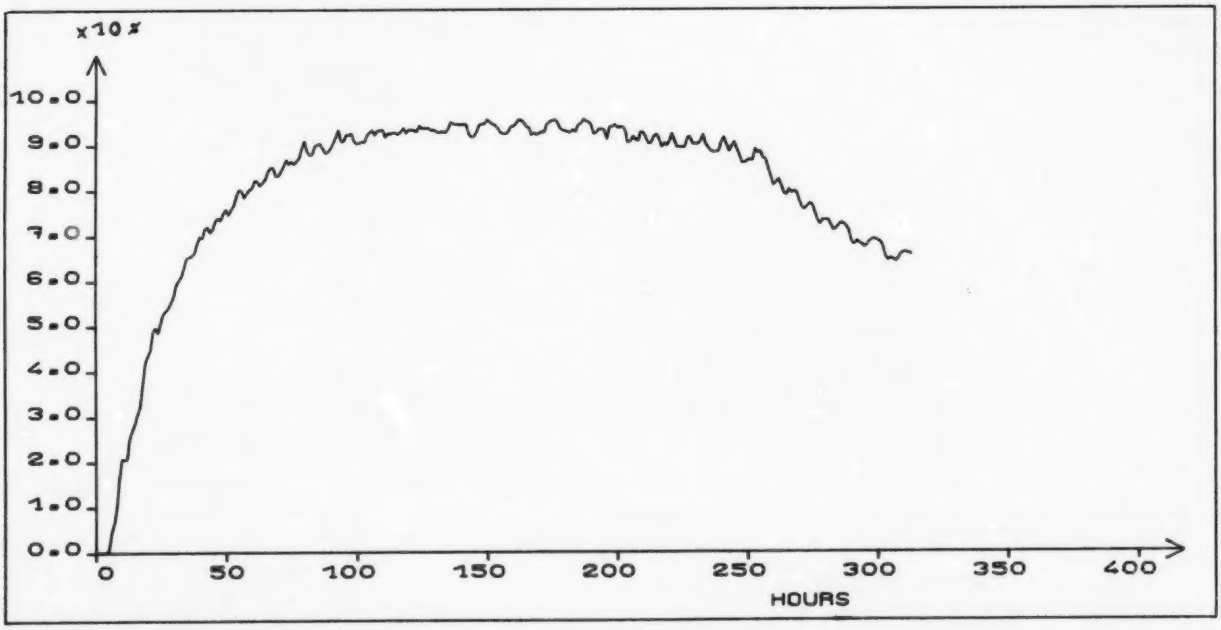

Fig. 5 : Evolution du maximum de différence relative entre la population perturbée et la population non-perturbée dans le cas où les dispersants sont appliqués.

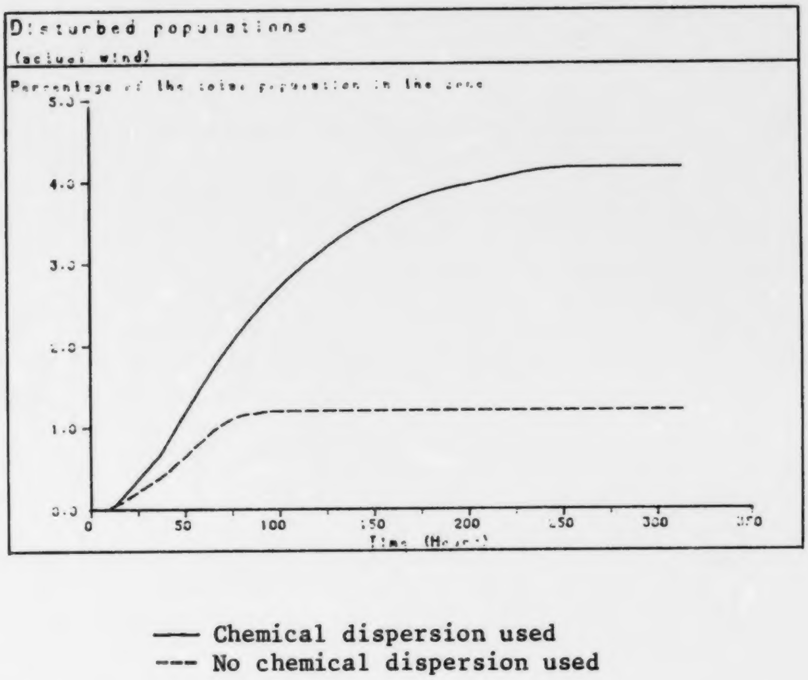

Fig. 6 : Impact net (pourcentage d'individus détruits par rapport à la population totale dans la zone considérée)

L'analyse des résultats complets de cette étude d'impact a permis de tirer les conclusions suivantes :

- L'usage des dispersants réduit sensiblement le volume de la nappe de surface.
- L'extension finale de la nappe varie peu d'un cas à l'autre. L'épaisseur de la nappe est donc plus faible lorsqu'il est fait usage des dispersants, ce qui implique une réduction de l'efficacité de la récupération mécanique dans ce cas.
- L'usage des dispersants accroît l'impact sur le zooplancton. Dans le cas présent, il est 3,5 fois plus important.

LE SYSTEME "ATMOS"

Le second système présenté ici concerne les produits chimiques qui forment une nappe à la surface de la mer et dont une fraction importante s'évapore. Il s'agit, par exemple, du toluène ou du benzène qui sont respectivement les deuxième et troisième produits chimiques les plus transportés par voie maritime.

Ce projet est pour le moment au stade de la conception. Il a pour but d'assister les pouvoirs publics dans leurs interventions contre les pollutions chimiques dangereuses. Les produits chimiques visés - flottants et volatils - présentent en effet un danger immédiat pour la santé de l'homme, danger augmenté par la persistance de la source à la surface de la mer. La réalisation s'articulera sur quatre points :

- Adaptation d'un modèle de comportement des nappes en surface, notamment en généralisant le terme d'évaporation.
- Adaptation d'un modèle de dispersion atmosphérique au milieu marin : paramétrisation de la couche limite et prise en compte d'un terme source qui se déplace et s'étale.
- Couplage des deux modèles précités.
- Insertion des modèles dans un système interactif et convivial.

Dans son ensemble, la philosophie du système ATMOS sera très proche de celle du système OPIA, tant par sa conception modulaire que par son utilisation.

DISCUSSION

Les deux systèmes présentés ici sont destinés à apporter une aide efficace aux équipes opérationnelles s'occupant de pollutions en mer, tant à l'entraînement que lors de cas réels. Ils constituent des systèmes homogènes et intégrés simulant l'évolution de polluants présents sous deux phases distinctes : phase liquide et phase dispersée/dissoute dans l'un, phase liquide et phase gazeuse dans l'autre.

Ils constituent un progrès par rapport aux situations antérieures car l'accent a été mis sur la facilité d'exploitation de modèles sophistiqués. Ce but est atteint en simplifiant les opérations à exécuter par l'opérateur, en réduisant les possibilités d'erreur et, surtout, en garantissant la compréhension des résultats par l'usage extensif de facilités graphiques.

L'expérience actuelle du système OPIA montre qu'ainsi conçu, il permet de répondre à de nombreuses questions visant à améliorer la lutte entre les pollutions en mer, par exemple pour une pollution donnée :

- Est-il opportun d'utiliser des dispersants ?
- Quelle est la meilleure combinaison entre les moyens chimiques et les moyens mécaniques ?
- Si on les utilise, à quel moment faut-il appliquer les dispersants pour obtenir l'effet maximum tout en minimisant l'impact ?

Dans l'état actuel des connaissances, ces systèmes sont des outils importants pour l'optimalisation de la lutte contre les pollutions en mer. Ils ne constituent néanmoins qu'une étape vers la constitution de systèmes permettant de prendre en compte l'immense variété des produits chimiques transportés par voie maritime.

REMERCIEMENTS

La réalisation des deux systèmes présentés ici est supportée financièrement par l'Etat belge et la Commission des Communautés Européennes, Direction Générale de l'environnement, de la protection des consommateurs et de la sécurité nucléaire.

"DEW LINE '85'"
PCB Clean-up

by A. Holtz, and M. A. Sharpe
Environmental Protection Service

Abstract

The Distant Early Warning (DEW) Line, is a series of radar stations spread across Canada's arctic lands between the Arctic Circle and 70°N latitude. The stations were constructed by the United States and Canadian militaries in the 1950s, to act as an early warning system.

When parts of the system and its equipment became obsolete in the mid-1960s, 22 of the 42 stations were abandoned. Because the sites were isolated, clean-up and removal of the equipment would have been both difficult and expensive. As a result, the buildings and much of the equipment were left at the abandoned sites.

As environmental awareness in Canada's north increased, concern arose over potential hazardous materials remaining at the DEW Line sites (UMA, 1982).

In 1984, Environment Canada conducted two field survey programs at nine DEW Line stations to assess the state of the sites and to facilitate an estimate of the amount of hazardous material remaining at all of the abandoned sites. The results of these surveys indicated that considerable amounts of hazardous material, including some polychlorinated biphenyl (PCB) contaminated materials remained at the sites.

Based on Environment Canada's findings, the Department of Indian Affairs and Northern Development (DIAND) and the Department of National Defense (DND) agreed to conduct a clean-up and removal of hazardous materials at all abandoned DEW Line sites. Also, a community consultation process was initiated by DIAND to inform the northern population of what was taking place.

This paper will discuss the significance of the hazardous material, present the findings of the original surveys and summarize the action taken to clean-up the sites.

Introduction

The original Canadian DEW Line system built in 1957 consisted of 42 sites located across Canada's Arctic from the Alaska/Yukon border to the east side of Baffin Island (FIGURE 1). There were three distinct types of installations: main, auxiliary and intermediate sites. A main site (FIGURE 2) consisted of five 30-foot, two 60-foot, and two 120-foot parabolic antennae, one 25-foot UHF tower, a rotating radar, building trains of up to 25 modules, four 250,000-gallon POL (petroleum, oil, lubricants) tanks, five warehouses, a recreation building and several garage/storage buildings. An auxiliary site (FIGURE 3) consisted of several antennae, a rotating radar, one 25-module building train, one garage, one warehouse and four 65,000-gallon POL tanks. An intermediate site (FIGURE 4) consisted of a single five-module building train, one warehouse, one garage, one Inuit house, one Doppler tower, and, usually, four 20,000-gallon POL tanks (Andzan, 1985).

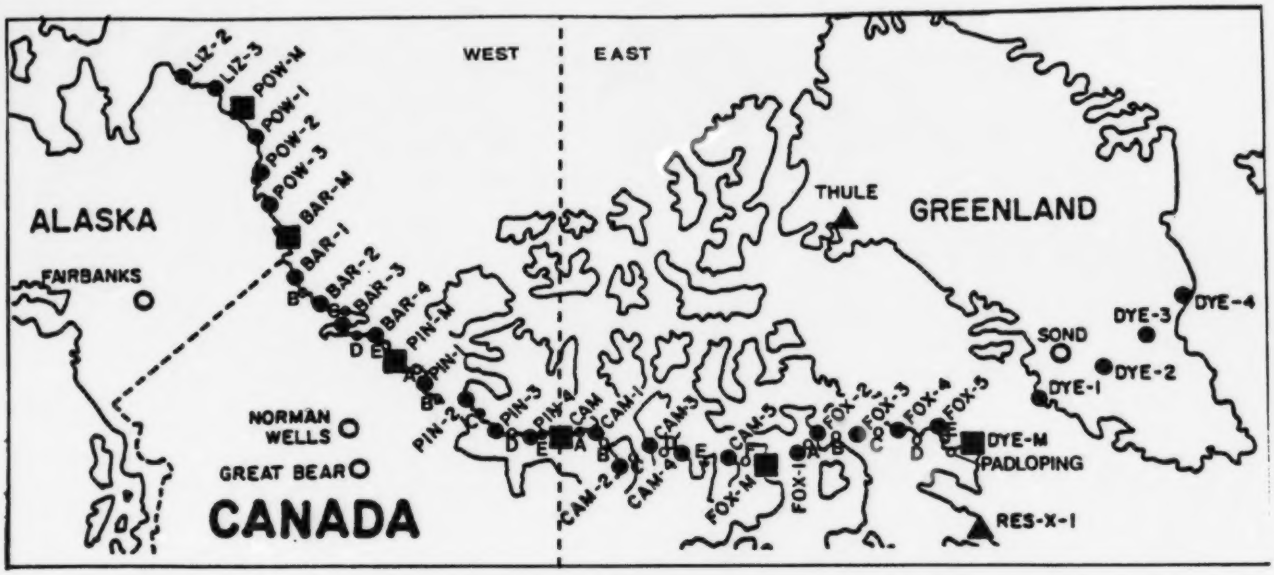
WEST
EAST
ALASKA
FAIRBANKS
NORMAN WELLS
GREAT BEAR
CANADA
GREENLAND
THULE
SOND
LIZ-2
LIZ-3
POW-M
POW-1
POW-2
POW-3
BAR-M
BAR-1
BAR-2
BAR-3
BAR-4
PIN-M
PIN-1
PIN-2
PIN-3
PIN-4
CAM
CAM-1
CAM-2
CAM-3
CAM-4
CAM-5
FOX-M
FOX-1
FOX-2
FOX-3
FOX-4
FOX-5
DYE-M
DYE-1
DYE-2
DYE-3
DYE-4
PADLOPING
RES-X-1
A
B
C
D
E
F

FIGURE 1: DEW Line Stations in the Canadian Arctic

Canadian Active Stations

BAR 1	Komakuk Beach
BAR 2	Shingle Point
BAR 3	Tuktoyaktuk
BAR 4	Nicholson Peninsula
PIN M	Cape Perry
PIN 1	Clifton Point
PIN 2	Cape Young
PIN 3	Lady Franklin
PIN 4	Byron Bay
CAM M	Cambridge Bay
CAM 1	Jenny Lind Island
CAM 2	Gladman Point
CAM 3	Shepard Bay
CAM 4	Pelly Bay
CAM 5	Mackar Inlet
FOX M	Hall Beach
FOX 2	Longstaff Bluff
FOX 3	Dewar Lakes
FOX 4	Cape Hooper
FOX 5	Broughton Island
DYE M	Cape Dyer

Canadian Abandoned Stations

BAR B	Stokes Point
BAR C	Tununuk
BAR D	Atkinson Point
BAR E	Horton River
PIN A	Pearce Point
PIN B	Clifton Point
PIN C	Bernard Harbour
PIN D	Ross Point
PIN E	Cape Peel
CAM A	Sturt Point
CAM B	Hat Island
CAM C	Matheson Point
CAM D	Simpson Lake
CAM E	Keith Bay
CAM F	Sarcpa Lake
FOX 1	Rowley Island
FOX A	Bray Island
FOX B	West Baffin
FOX C	Ekalugad Fjord
FOX D	Kivitoo
FOX E	Durban Island
	Padloping Island

■ Main DEW Line Stations
▲ Auxiliary Stations
o Abandoned Sites

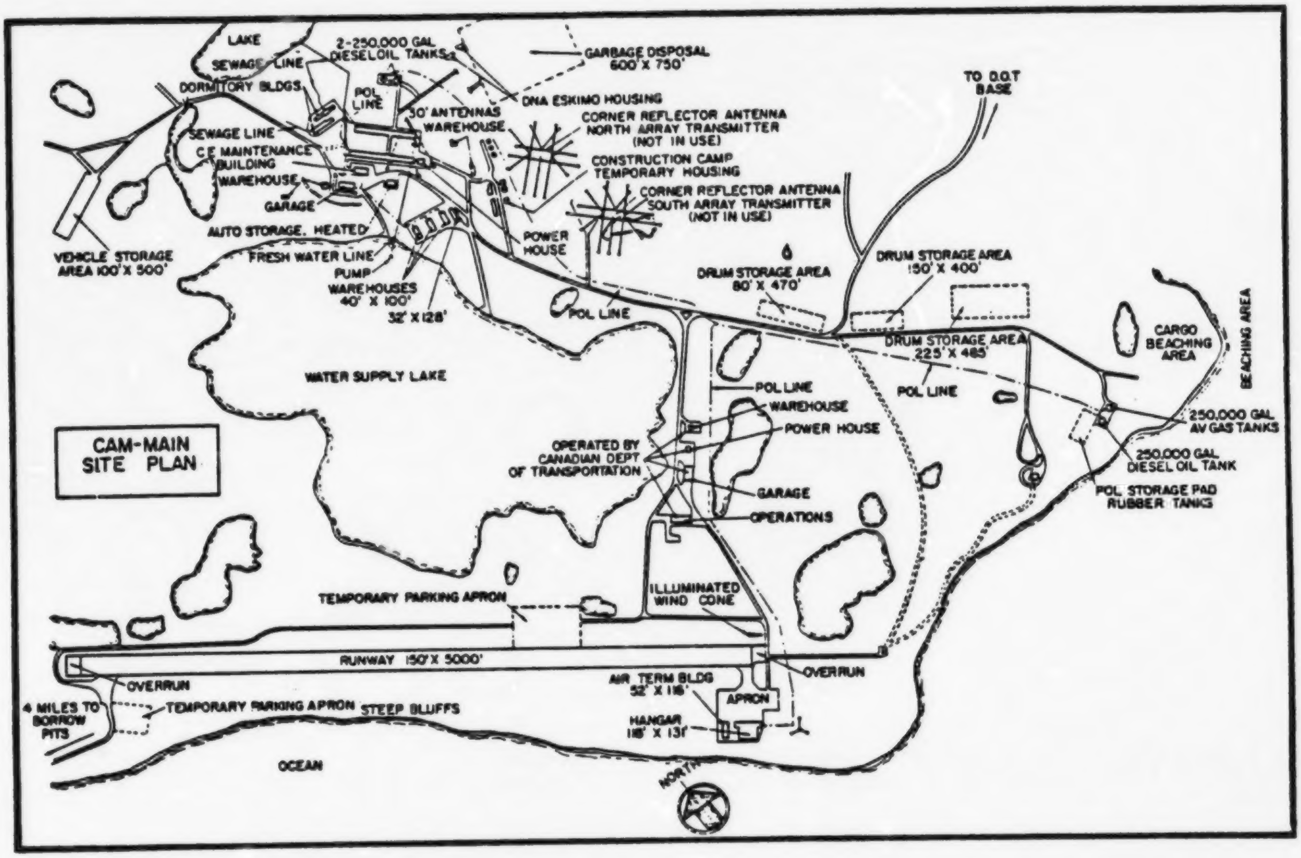
LAKE
2-250,000 GAL DIESELOIL TANKS
GARBAGE DISPOSAL 600' X 750'
SEWAGE LINE
DORMITORY BLDGS
POL LINE
DNA ESKIMO HOUSING
TO D.O.T BASE
30' ANTENNAS
WAREHOUSE
CORNER REFLECTOR ANTENNA NORTH ARRAY TRANSMITTER (NOT IN USE)
SEWAGE LINE
C.E MAINTENANCE BUILDING
CONSTRUCTION CAMP TEMPORARY HOUSING
WAREHOUSE
GARAGE
CORNER REFLECTOR ANTENNA SOUTH ARRAY TRANSMITTER (NOT IN USE)
AUTO STORAGE, HEATED
POWER HOUSE
VEHICLE STORAGE AREA 100' X 500'
FRESH WATER LINE
PUMP
WAREHOUSES 40' X 100'
32' X 128'
DRUM STORAGE AREA 80' X 470'
DRUM STORAGE AREA 150' X 400'
POL LINE
DRUM STORAGE AREA 225' X 465'
CARGO BEACHING AREA
BEACHING AREA
WATER SUPPLY LAKE
POL LINE
POL LINE
WAREHOUSE
250,000 GAL AV GAS TANKS
POWER HOUSE
CAM-MAIN SITE PLAN
OPERATED BY CANADIAN DEPT OF TRANSPORTATION
250,000 GAL DIESEL OIL TANK
GARAGE
POL STORAGE PAD RUBBER TANKS
OPERATIONS
TEMPORARY PARKING APRON
ILLUMINATED WIND CONE
RUNWAY 150' X 5000'
OVERRUN
OVERRUN
AIR TERM BLDG 52' X 116'
4 MILES TO BORROW PITS
TEMPORARY PARKING APRON
STEEP BLUFFS
APRON
HANGAR 118' X 131'
OCEAN
NORTH

FIGURE 2 - SITE PLAN OF A MAIN SITE

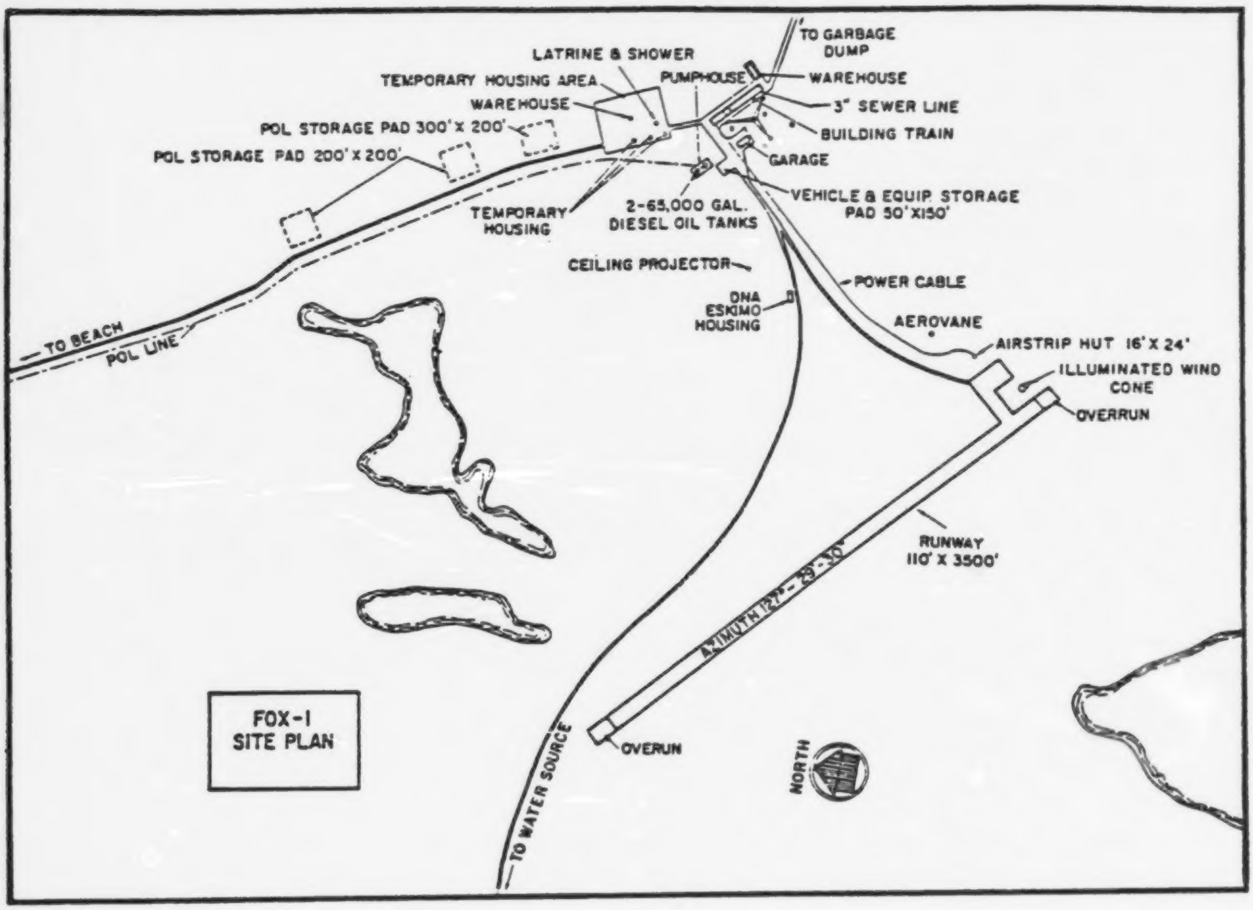
TO GARBAGE DUMP
LATRINE & SHOWER
TEMPORARY HOUSING AREA
PUMPHOUSE
WAREHOUSE
WAREHOUSE
3" SEWER LINE
POL STORAGE PAD 300' X 200'
BUILDING TRAIN
POL STORAGE PAD 200' X 200'
GARAGE
VEHICLE & EQUIP. STORAGE PAD 50' X150'
TEMPORARY HOUSING
2-65,000 GAL. DIESEL OIL TANKS
CEILING PROJECTOR
POWER CABLE
DNA ESKIMO HOUSING
AEROVANE
AIRSTRIP HUT 16' X 24'
ILLUMINATED WIND CONE
OVERRUN
TO BEACH
POL LINE
RUNWAY 110' X 3500'
AZIMUTH 127° - 29'-30"
FOX-1 SITE PLAN
OVERUN
TO WATER SOURCE
NORTH

FIGURE 3 - SITE PLAN OF AN AUXILIARY SITE

All sites contained a gravel airstrip, gravel roads, and fuel storage areas supported by one-metre thick gravel pads.

Of the 22 sites in this clean-up, two were auxiliary sites and 20 were intermediate sites.

Hazardous Materials at DEW Line Sites

Based on information obtained from USAF records (Andzan, 1985) a list was constructed of waste materials which could have remained at the sites (TABLE 1).

TABLE 1

Hazardous Materials at DEW Line Sites

- waste oil
- PCB transformers/capacitors
- asbestos
- sewage
- lead-based paints
- radioactive tubes
- scrap metal
- radar components
- fuel drums
- lime
- antifreeze
- wood
- AVGAS (aviation fuel)
- sulfamic acid
- cathode ray tubes and screens
- filtron tubes
- oscillators
- meters
- copper wire
- transmission fluid
- 1-1-1-trichloroethane
- PBX telephone equipment
- mercury vapour rectifier tubes
- paint thinners
- batteries
- chlorinated hydrocarbons
- corrosion inhibitors
- lye
- corrosives
- paper
- plastics
- solvent
- dynamite
- RF interference filters
- generators
- scopes
- vehicles
- rubber fuel bladders

The first confirmation that at least some of these materials were indeed present resulted from an inspection of Fox Sector (Hall Beach to Cape Dyer) DEW Line facilities carried out in 1981 (EPS, 1981). PCB equipment was identified and inventoried as to location, type, size and condition. POL tanks at some sites still retained their original contents and stockpiles of fuels, solvents and lubricating oils existed. In additon, the sites were often strewn with assorted metal and wood debris.

A complete inventory of PCB equipment at all active DEW Line facilities was reported to EPS by DND in 1981, and in 1982/83, a clean-up program was initiated by the United States to remove this material. Concurrently, EPS initiated a program to identify hazardous materials at all the abandoned sites by including them in a contracted review of active and abandoned landfills in the Northwest Territories (UMA, 1982). This review, however, did not involve actual site visits.

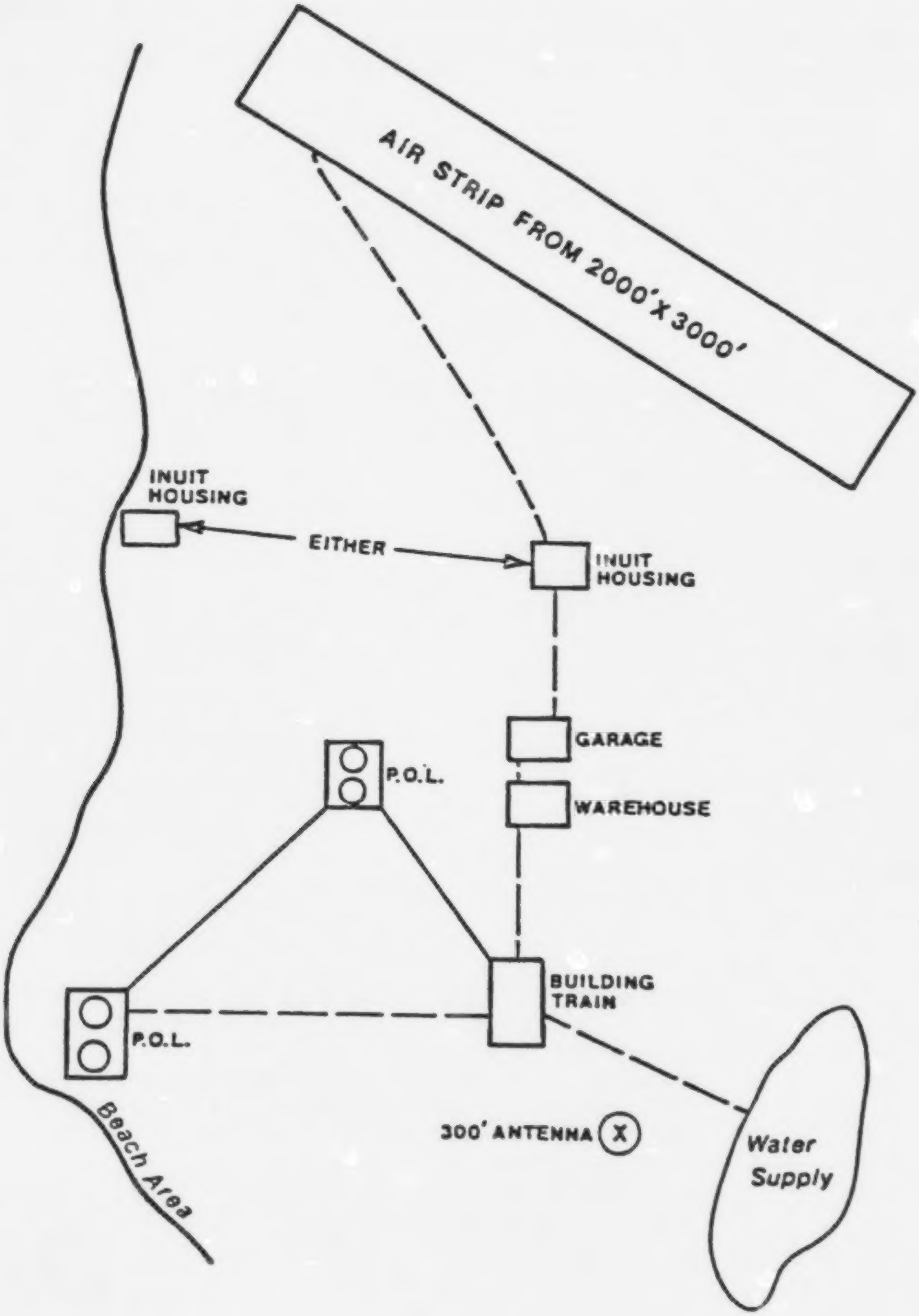
AIR STRIP FROM 2000' X 3000'
INUIT HOUSING
EITHER
INUIT HOUSING
GARAGE
WAREHOUSE
P.O.L.
BUILDING TRAIN
P.O.L.
300' ANTENNA
X
Water Supply
Beach Area

FIGURE 4 - SITE PLAN OF AN INTERMEDIATE SITE

Consequently, in July, 1984, the Environmental Protection Service (EPS) surveyed five abandoned DEW Line sites in the central Arctic. Sites investigated were all within 400 km of Cambridge Bay and included: Hat Island (CAM B), Sturt Point (CAM A), Cape Peel (PIN E), Ross Point (PIN D) and Bernard Harbour (PIN C). Objectives of the investigation were: to inventory and report environmental conditions at the sites; to determine the extent of environmental problems; and to provide a basis for recommendations for future action at the 22 abandoned sites (Holtz and Sharpe, 1984).

The investigations revealed that one site had all buildings intact; two of the sites had intact building trains, with only the foundations of the warehouse and garage remaining; and two sites had only building foundations remaining. At the three sites where the building train was still standing, four large cabinets containing PCB-filled electrical equipment were found in the communications room. At four sites, small capacitors were also found on the ground outside of the buildings. While much of the equipment seemed to be undisturbed and in good condition, the capacitors on the ground were corroded and leaking. Analysis revealed that these capacitors contained the PCB compound Aroclor 1254 (84% pure) and that the surrounding soil was contaminated. The buildings also contained generators and fluorescent light ballasts (PCB-containing) along with other debris.

Each site having intact buildings and electrical cabinets was estimated to have 1500 kg of equipment containing 305 litres of PCB fluid. Extrapolating these figures to include all 22 abandoned sites yielded a maximum estimate of 33,000 kg and 6700 litres of PCB fluid. At those sites that were not intact, the PCB-containing equipment possibly had been scattered with the debris, buried, salvaged by the armed forces or scavenged.

Radioactivity detectors were used in the investigation, and no radioactive materials of any kind were detected or observed.

Observations at the five sites confirmed the presence of the following other wastes: building debris; and empty or partially filled, and leaking, drums of diesel fuel, lubricating oils and solvents. There was evidence at two sites of recent use by hunters or fishermen, and evidence of site use by numerous bird and wildlife species.

A further six sites in the western Arctic were investigated in September, 1984. These investigations produced similar information to that obtained in the first survey.

Based on this confirmation of the presence of significant quantities of hazardous materials, particularly PCB-containing electrical equipment, EPS recommended that the federal government conduct a clean-up of these sites. A national committee consisting of representatives from the Department of Indian and Northern Affairs (DIAND), the Department of National Defence (DND), Environmental Protection Service (EPS) and National Health and Welfare (NH&W) assigned responsibilities for clean-up activities, namely:

(a) DIAND to lead and coordinate community liaison work;
(b) DND to plan logistics, supply personnel and materials, and oversee the clean-up and removal of hazardous materials;
(c) EPS to provide clean-up procedures; training in handling and safety procedures for the clean-up crews; onsite advice during clean-up and supervision of equipment removal.

1985 Clean-up Operation Methods

The clean-up operation at the 22 abandoned stations was scheduled for the period of 17 July to 10 September, 1985. Two clean-up crews were formed to conduct the operation: one starting in the western Arctic at Inuvik and one in the eastern Artic at Cape Dyer. Each clean-up crew consisted of seven military personnel, one Environment Canada representative, and one DIAND representative. A second Environment Canada representative and a National Research Council advisor assisted both work crews in establishing clean-up procedures. Each crew was supported by two Twin Huey helicopters and a Buffalo aircraft supplied by DND.

A training session preceded crew movements to the eastern and western Arctic. Personnel were briefed on the properties and control of PCBs; safe handling of PCB-containing equipment; spill contingency plans; anticipated site conditions, and types and quantities of material expected. Each clean-up crew was provided with site maps and complete written procedures.

A reconnaissance of each site, by the crew commander and advisors, was conducted prior to crew deployment to establish on-site procedures and determine equipment needed for the removal of hazardous materials. Upon arrival at each site, the entire crew, walking at 10 pace intervals, swept the site, marking with stakes points where equipment, barrels, suspect spills or burial sites were present. These were also marked on the site map.

The military crew proceeded to remove and package easily-identified PCB-containing equipment from the buildings. The equipment was inventoried, wrapped in heavy plastic (6 mil), placed in 45-gallon drums containing 5-7 cm. of absorbent material, and sealed. Loose equipment found outside buildings was treated similarly, while equipment too large to be accommodated in a drum was wrapped in plastic and placed on absorbent material in an Enviropac container (FIGURE 5). This is a commercially available, palletized, 16-gauge steel sealable container, recommended for secondary containment of hazardous materials by the United States Environmental Protection Agency. Where the equipment content could not be confirmed as PCBs, the equipment was removed and handled as if confirmation had been made. Each drum was marked with a serialized EPS Hazard Warning Label, and placed with 3 other drums in an Enviropac container which was marked with PCB warning labels.

The DND Crew Commander and the EPS, DIAND and NRC representatives proceeded with detailed site inventory and soil sample collection and testing at suspect spill and burial sites.

Soils were tested on-site for PCB content or presence, either using a field test kit or by odour (PCB/TCB mixtures can be detected by smell at 1-5 ppm). The field test kit was one which had been developed for EPS by Enviro-Test Laboratories. It is based on thin layer chromatography of extracted organo-chlorine compounds and has a detection limit of approximately 10 ppm.

Soil PCB levels were reported on site maps, while the visibly stained area was marked with paint. Soil was then removed to about 7 cm. beyond the outline, and to a depth of approximately 30 cm. Further testing was conducted and more soil removed as necessary. The contaminated soil was placed in 45-gallon drums, and then into Enviropacs, while clean gravel from elsewhere on the site was used to fill the hole.

Confirmatory soil samples were taken and stored in tinfoil and plastic bags for subsequent gas chromatographic analysis. Such samples were also taken at sites of suspected burial of PCB-containing equipment.

Concurrently, designated military personel conducted the inventory and destruction of POL. Clean-up of non-hazardous waste and debris remaining at the sites will be conducted in future by DIAND in cooperation with the Government of the Northwest Territories.

Filled drums and Enviropacs were flown back to main staging areas each day, for interim storage until the containers were consolidated at Hall Beach. In September, all filled containers were transshipped to the United States by U.S. military personnel for ultimate disposal.

Results and Discussion

In total, 134 drums containing 2681 pieces of PCB-containing equipment and contaminated soil were removed from the 22 sites (TABLE 2) during a period of 40 days.

Although adjustments were made to procedures because of individual site conditions and remote locations, generally speaking the planned procedures worked satisfactorily. The reconnaissance of a site by commander and advisors prior to crew deployment was found to be of paramount importance in ensuring that procedures could be properly modified. Good prior planning, especially on the part of the military, resulted in the safe and efficient movement of personnel, equipment and waste. The weather was cooperative, and only minor delays resulted from it and equipment breakdown.

The PCB soil test kit appeared to be unreliable, possibly due to cold air temperatures and inexperience of the operators. A complete evaluation of the test kits will be conducted at a later date.

Since only visible PCB equipment was removed from the sites, only eight of them may be considered free of PCB material. Fourteen sites were identified as having possible burial sites of PCB-containing equipment. Further consideration of actions pertaining to these sites must await the results of soil analyses and assessment of the significance of the environmental risk.

TABLE 2

Barrels of Materials from Abandoned Sites

Location	Numbers of Pieces of Equipment	Numbers of Barrels
Stokes Point	1	
Tununnik	6	2
Atkinson Point	68	6
Horton River	157	8
Pearce Point	171	8
Clifton Point	158	7
Bernard Harbour	142	6
Ross Point	145	8
Cape Peel	14	1
Sturt Point	2	Included in Hat Island
Hat Island	148	6
Matheson Point	9	3 (2 miscellaneous)
Simpson Lake	134	7
Keith Bay	97+	7
Sarcpa Lake	148	8
Rowley Island	369	12
Bray Island	171	8
West Baffin	209	9
Ekalugad Fjord	166	9
Kivitoo	48	5
Durban Island	214	9
Padloping Island	104	5
TOTAL	2,681	134

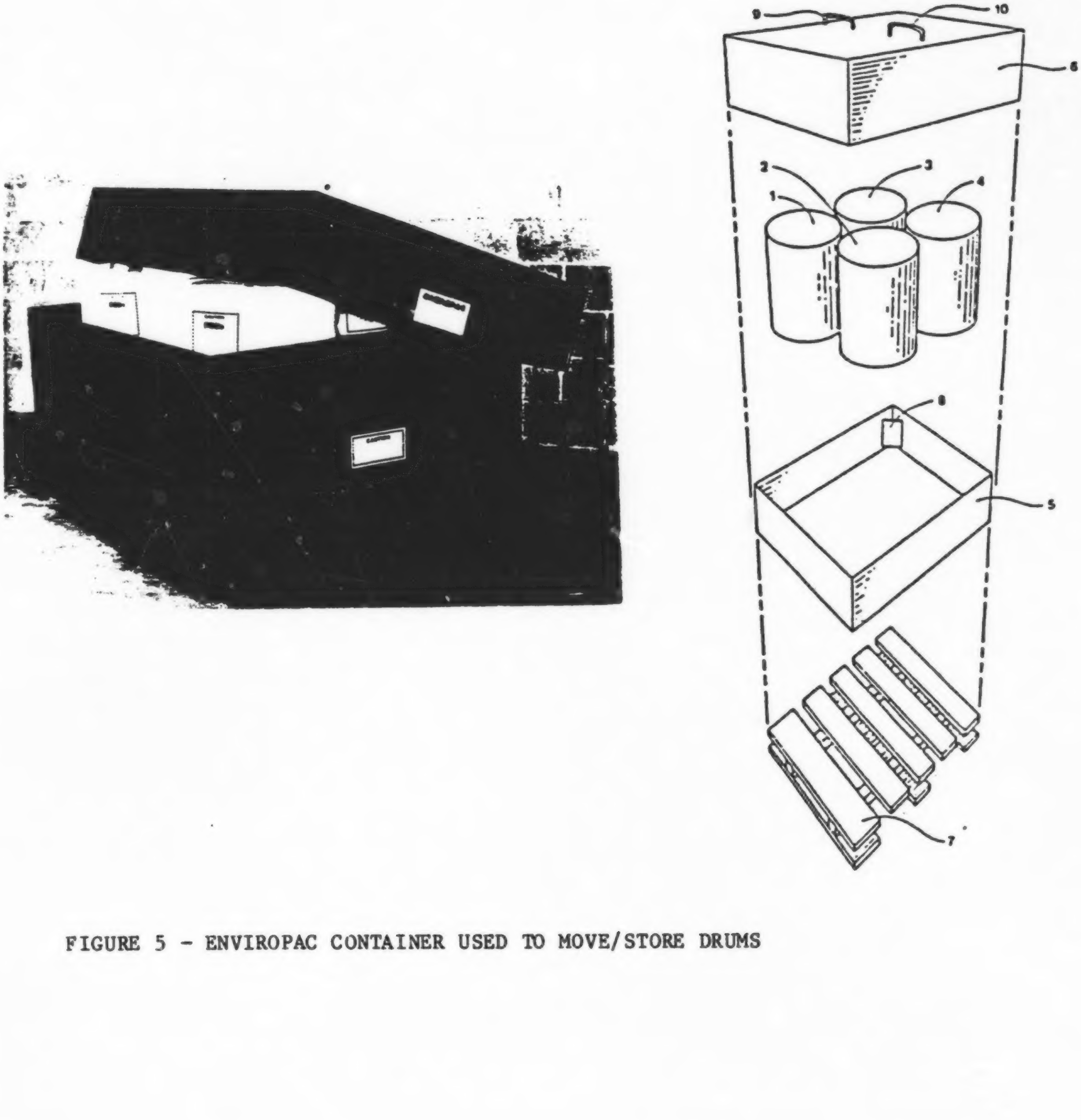
9
10
6
2
3
1
4
8
5
7

FIGURE 5 - ENVIROPAC CONTAINER USED TO MOVE/STORE DRUMS

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